Bull. Chem. Soc. Jpn., **69**, 751—764 (1996)

Solvent Effects on Anchimerically Assisted Solvolyses. III.[1] Solvent Effects on the Solvolyses of (1-Arylcycloalkyl)methyl *p*-Toluenesulfonates

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(Received September 29, 1995)

The solvolysis rates of (1-arylcyclobutyl)methyl and (1-arylcyclopropyl)methyl *p*-toluenesulfonates were measured in a wide variety of solvents. The aryl-assisted k_Δ solvolysis of [1-(*p*-methoxyphenyl)cyclobutyl]methyl *p*-toluenesulfonate did not give a linear Winstein–Grunwald correlation using the 2-adamantyl-based Y_{OTs} scale, but did show dispersion for different binary solvent mixtures. An extended dual-parameter treatment, $\log(k/k_{80\mathrm{E}}) = m_c Y_{\mathrm{OTs}} + m_\Delta Y_\Delta$, successfully correlated the present set of k_Δ solvolyses with $R > 0.995$ and $\mathrm{SD} < 0.09$. The blending parameter M_Δ $(= 0.51m_\Delta/(m_c+0.51m_\Delta))$ increases monotonically with increased electron donation by the substituent, showing an increased dispersion of the Y_{OTs} plot with increasing anchimeric assistance. The solvolysis of (1-arylcycloalkyl)methyl *p*-toluenesulfonates demonstrates the varying extent of anchimeric assistance by the neighboring groups, from a completely synchronous aryl-assisted process for the *p*-methoxy derivative of (1-phenylcyclobutyl)methyl *p*-toluenesulfonate, via moderately to weakly aryl-assistance by the *p*-methyl derivative and the unsubstituted compound, to a completely aryl-unassisted k_c process for the more electron-withdrawing aryl derivatives and the (1-arylcyclopropyl)methyl *p*-toluenesulfonates. The dual-parameter equation enables one to monitor the varying extent of anchimeric assistance in the transition state. From the results we propose a general solvolysis framework involving a continuous spectrum of k_c–k_Δ mechanisms for anchimerically assisted solvolysis.

The Winstein–Grunwald Equation (Eq. 1) and its extended form (Eq. 2) have been widely utilized as mechanistic probes for characterizing solvolytic processes:[2—5]

$$\log(k/k_{80\mathrm{E}}) = mY_{\mathrm{OTs}} \tag{1}$$

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

In Eqs. 1 and 2, k is the rate constant for the solvolysis of an organic tosylate (OTs; *p*-toluenesulfonate) in any solvent and $k_{80\mathrm{E}}$ is the corresponding rate constant in 80% v/v aqueous ethanol (80E); m is the sensitivity of the solvolysis rate to the solvent ionizing-power parameter (Y_{OTs}), and l is its sensitivity to the solvent nucleophilicity parameter (N_{OTs}).

We have found that, contrary to what has been pointed out,[5,7] the rate constants for the neophyl(2-methyl-2-phenylpropyl) (**1**) and other relevant k_Δ solvolyses, which should be free of nucleophilic solvent assistance, were not correlated[6] with the Y_{OTs} parameter defined by the k_c solvolysis of 2-adamantyl tosylate (**2**). It seemed to us that a Winstein–Grunwald type treatment of the solvent effects in such aryl-assisted solvolyses requires the application of an alternative scale of solvent polarities, which would be characteristic of k_Δ solvolyses.[1,6] Furthermore, the deviations from linearity when using Eq. 1 can serve as a probe for estimating the degree of aryl participation. This approach is parallel to the use of Eq. 2 for detecting the involvement and estimating the extent of the solvent nucleophilicity.[2b,2d,5]

Schadt, Bentley, and Schleyer pointed out that aryl substrates which yield resonance-stabilized carbenium ions do not give satisfactory correlations with the extended Winstein–Grunwald Equation (Eq. 2), and that Eq. 2 should not be applied for correlating solvolyses involving anchimeric assistance.[5] It has recently been suggested that the wide scope of dispersion observed for different binary solvent mixtures with significantly reduced m values in correlations of the solvolysis of neophyl-type substrates with Eq. 1 or Eq. 2 may be caused by aryl-bridging, or by charge-delocalizing conjugation between an aryl ring and the incipient carbenium center in the transition state.[1,6] The transition state for aryl-assisted ionization is stabilized by π-delocalization, and the accompanying cationic charge dispersal may remarkably reduce the sensitivity (i.e., the m value) to the solvent polarity, resulting in a significant loss of the highly oriented nucleophilic solvent molecules at the reaction center. This effect may differ for different binary solvent mixtures, leading to the observed dispersion.

We have proposed a new similarity comparison analysis of solvent effects for anchimerically aryl-assisted solvolyses (Eq. 3),[1,8]

$$\log(k/k_{80\mathrm{E}}) = m_c Y_{\mathrm{OTs}} + m_\Delta Y_\Delta \tag{3}$$

In this analysis, the solvolyses of 2-adamantyl-OTs (**2**) and *p*-methoxyneophyl-OTs (**1A**) model, respectively, the k_c and k_Δ mechanistic extremes, for substrates potentially capable of undergoing neighboring group assistance. The adjustable blending parameters (m_c and m_Δ) reveal the extent to which the solvolysis of a substrate approaches, respectively, the essentially unassisted (open ion) k_c model **2** (m_Δ=0) or the entirely aryl-assisted (bridged ion) k_Δ model **1A** (m_c=0).

For establishing the validity of this analysis, it is essential to examine the applicability of Eq. 3 to a wide range of anchimerically assisted solvolyses. Consequently, we deal in the present paper with a series of solvolyses of β-arylalkyl tosylates having a neophyl-type structure. For these systems, which include substituted neophyl **1**, ring-substituted (1-phenylcyclobutyl)methyl (**3**) and (1-phenylcyclopropyl)methyl tosylates (**4**), a competitive solvent-assisted (k_s) route is unlikely due to a structural reason. For a comparison, we also investigate the solvolysis of the parent neopentyl(2, 2-dimethylpropyl) (**5**) and cyclopropylmethyl tosylates (**6**) (Chart 1).

The substituent effect of the solvolyses of these sulfonates can be generally described by the Yukawa–Tsuno Equation,[9)]

$$\log(k/k_o) = \rho(\sigma^\circ + r\Delta\bar{\sigma}_R^+), \qquad (4)$$

where σ° is the normal substituent constant, which does not involve any additional π-electronic interaction between the substituent and the reaction center, and $\Delta\bar{\sigma}_R^+$ is the resonance substituent constant measuring the capability for π-delocalization of the π-electron donor substituent, which is defined by $\sigma^+ - \sigma^\circ$.[9b)] The r value is a parameter characteristic of a given reaction, measuring the extent of resonance demand, i.e., the degree of resonance interaction between the aryl group and the reaction site in the rate-determining transition state. An analysis of the substituent effect by Eq. 4 had led to the conclusion that in the solvolyses of (1-arylcyclobutyl)methyl p-bromobenzenesulfonates(brosylates) **3**-OBs, the β-aryl-assisted mechanism characterized by an intermediate r value of ca. 0.6, occurs only for substrates carrying strongly electron-donating substituents on the aryl ring.[10)] The nonlinear Yukawa–Tsuno plot is shown in Fig. 1. A gradual change in the aryl-unassisted mechanism having a diminished r value occurs for the range of systems carrying electron-attracting substituents.[10)] In contrast, the solvolysis of (1-arylcyclopropyl)methyl tosylates **4** had shown an excellent linear correlation with Eq. 4, with r values of ca. 0.1, indicating an essentially unexalted resonance contribution.[10)] These differences in the magnitude of the resonance demand probe parameter (r) distinctly imply different degrees of π-delocalization in the transition states for the solvolyses of **3** and **4**. We expected that this difference may also be reflected in the dispersion behavior when correlating solvent effects in the solvolyses of **3** and **4**. However, since the literature data[11,12)] for these solvolyses in varying solvents are insufficient for an extensive comparison with the simple Schleyer–Bentley Y_{OTs} analysis,[5)] we collected much more data in the present work.

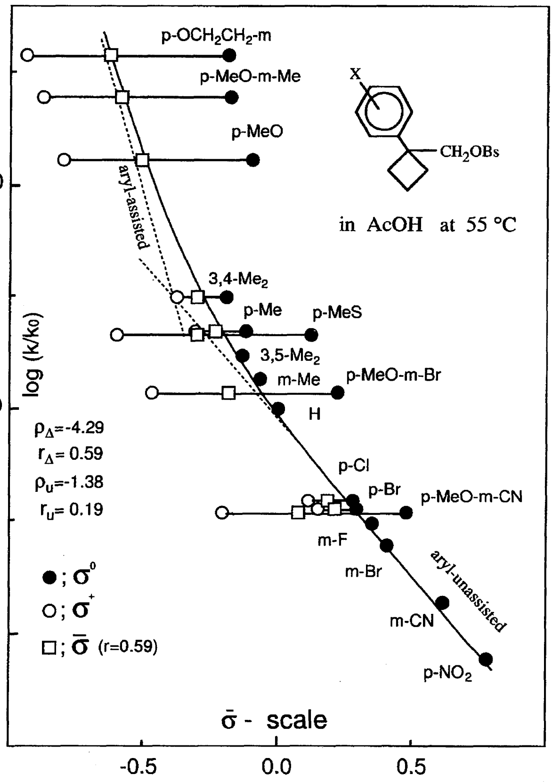


Fig. 1. Substituent effect on the acetolysis of (1-phenylcyclobutyl)methyl brosylates **3**-OBs at 55 °C.

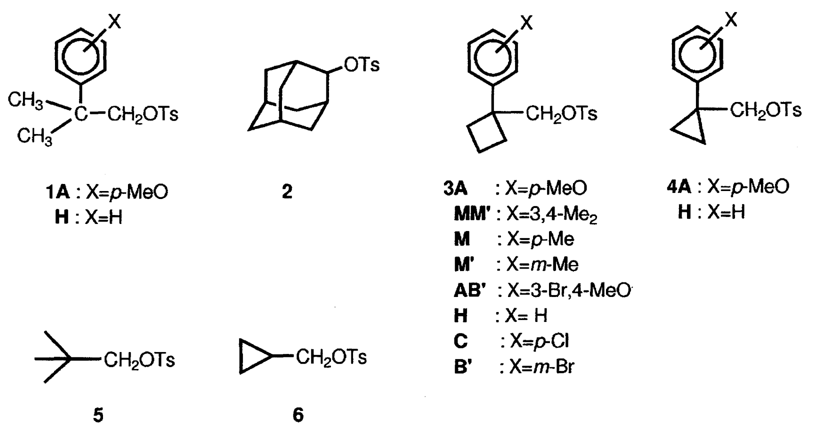


Chart 1.

Results and Treatment of Data

Solvolysis Data. The solvolysis rates of [1-(substituted phenyl)cycloalkyl]methyl tosylates, **3** and **4**, and the parent substrate **6** were determined in a wide variety of solvents, mostly by a conductimetric method, and are summarized in Tables 1 and 2. The ionizing power scale (Y_{OTs}) and the nucleophilicity scale (N_{OTs}) parameters employed for the correlations, and a set of solvent polarity scale (Y_{Δ}) parameters (not given) based on the solvolysis of p-methoxyneophyl tosylate **1A** were taken from our previous studies.[1,6,13,14]

Correlations with the Winstein–Grunwald Equation. The ordinary Winstein–Grunwald treatment using Eqs. 1 and 2 and the conventional Y_{OTs} and N_{OTs} parameters[1,4—6,13,14] has been applied to all of our solvolyses; the results are summarized in Table 3. A simple and extended analysis using the alternative reference (Y_{Δ}) scale (Eqs. 5 and 6)[1,6)]

$$\log(k/k_{80\mathrm{E}}) = m'Y_{\Delta} \tag{5}$$

$$\log(k/k_{80\mathrm{E}}) = m'Y_{\Delta} + lN_{\mathrm{OTs}} \tag{6}$$

was also applied to the same sets of data; the results are summarized in Table 4.

The $\log k$ vs. Y_{OTs} plots show varying degrees of disper-

Table 1. Solvolysis Rates of (1-Arylcyclobutyl)methyl Tosylates[a)]

Solvent[b)]	p-MeO (**3A**)	3,4-Me$_2$ (**3MM′**)	p-Me (**3M**)	m-Me (**3M′**)	3-Br-4-MeO (**3AB′**)	H (**3H**)	p-Cl (**3C**)	m-Br (**3B′**)
			—$k_t \times 10^5/\mathrm{s}^{-1}$ at 45 °C—					
100E	1.003	0.1933	0.1496	0.07980[c,d)]	0.0617[c,e)]			
90E	3.252	0.7280	0.4927	0.2492	0.2217[c,f)]	0.2161[c)]		
80E	6.013	1.556	1.066	0.600	0.4581	0.4897	0.2367	
70E	10.38	2.732	2.009	1.113	0.8184	0.9356	0.4288	
60E	16.05	4.739	3.525	2.062	1.481	1.767	0.7892	0.2748
50E	23.35	9.373	6.634	3.992	2.496	3.387	1.488	0.5625
40E	46.06	16.07	13.68	8.526	4.527	7.213	3.032	1.531
30E	88.70	41.17	33.95	19.68	10.40	17.75	8.474	3.524
80A	0.9792	0.2742	0.1947					
70A	2.495	0.6698	0.5449	0.3401	0.2280	0.2500	0.1228	
60A	5.363	1.689	1.299	0.8657	0.5500	0.7221	0.2723	
50A	11.78	3.787	3.104	2.154	1.185	1.737	0.7499	0.3137
40A	26.56	9.645	7.967	5.670	2.953	4.455	2.012	0.9406
30A	56.48	26.31	21.73	15.35	6.646	12.03	5.219	
MeOH	2.634	0.6909	0.4106	0.2331	0.2862			
80M	11.79	3.243	2.345	1.320	0.9073	1.021	0.4020	
60M	34.52	11.31	9.257	5.460	3.078	4.176	1.701	
50M	56.20	23.16	17.98	10.98	5.800	8.718	3.801	
80ET	2.446	0.5511	0.2987	0.1678[c,g)]	0.1676[c,h)]	0.07902[c,i)]		
60ET	6.299	1.422	0.8083	0.4180	0.3444	0.2626		
40ET	15.40	4.387	2.389	1.082	0.7983	0.8041	0.2362	
20ET	42.76	14.50	7.606	3.408	2.229	2.226	0.6247	
TFE	116.9	56.44	27.88	12.50	6.283	7.593	2.225	1.009
97Tw	89.59	39.91	22.60	10.10	5.612	6.374	1.794	
80T	71.64	32.67	18.90	9.201	4.900	6.074	1.780	0.9786
50T	74.56	34.71	22.00	11.70	5.212	8.350	2.699	1.417
40T			24.75	13.55	6.448			
30T	89.83	42.54	31.80	17.07	8.693	13.73	4.586	
97HFIPw	764.9	661.0	333.4	131.9	52.8	81.13	18.69	8.123
50HFIP	169.5	99.39				14.57		
AcOH	2.792[j)]							
50AF	70.70							
HCOOH	297.9	116				35.90		
80AN	2.833	0.8886	0.6598	0.4471	0.3162	0.3415		
60AN	8.646	3.034	2.372	1.586	1.014	1.307	0.5553	
50AN	14.64	6.741	4.420	3.149	1.921	2.605	1.054	0.4915

a) Conductimetrically determined, unless otherwise noted. b) Volume percent of first-named organic component, unless otherwise noted. Abbreviation, E=ethanol, A=acetone, M=methanol, AN=acetonitrile, T=TFE=2,2,2-trifluoroethanol, HFIP=1,1,1,3,3,3-hexafluoro-2-propanol, ET=ethanol–TFE mixtures (e.g., 20ET=20 vol EtOH : 80 vol TFE mixture), and 50AF (1 vol AcOH : 1 vol HCOOH). Suffix w means weight percent. c) Extrapolated from rate data at other temperatures. d) 0.3229×10^{-5} s^{-1} (55 °C), 4.154×10^{-5} s^{-1} (75 °C). e) 0.2557×10^{-5} s^{-1} (55 °C), 3.436×10^{-5} s^{-1} (75 °C). f) 0.7495×10^{-5} s^{-1} (55 °C), 6.943×10^{-5} s^{-1} (75 °C). g) 0.5872×10^{-5} s^{-1} (55 °C), 5.793×10^{-5} s^{-1} (75 °C). h) 0.5330×10^{-5} s^{-1} (55 °C), 4.414×10^{-5} s^{-1} (75 °C). i) 0.3040×10^{-5} s^{-1} (55 °C), 3.567×10^{-5} s^{-1} (75 °C). j) Titrimetrically determined.

Table 2. Solvolysis Rates of (1-Arylcyclopropyl)methyl and Cyclopropylmethyl Tosylates[a)]

Solv.[b)]	(**4**)		(**6**)
	p-MeO (**4A**)	H (**4H**)	
	$k_t \times 10^5/\mathrm{s}^{-1}$ at 25 °C		
100E	12.97	6.18	6.420
90E	74.56	34.86	61.85
80E	204.6	104.8	247.3
70E	430.5	230.0	646.8
60E	762.3	447.7	1550
50E	1490	946.0	
40E	3570		
30E	9830		
80A	32.44	15.78	
70A	103.0	51.66	160.4
60A	282.1	148.4	542.3
50A	786.5	429.0	
40A	2190	1260	
30A	5960		
MeOH	52.46	24.90, 25.7[c)]	28.38, 25.0[c)]
80M	429.1	227.4	399.1
60M	1930	1001	2800
50M	4130	2760	
80ET	30.46	13.95	12.68
60ET	78.44	37.40	
40ET	222.2	111.6	91.90
20ET	679.1		
TFE	2080	1360	1060
97Tw	1930	1170	1080
80T	2220	1310	1730
50T	2970	2060	
30T	5630	4970	
60D[d)]	232.3	116.8	407.7
80AN	106.2	51.54	119.9
60AN	441.1		
i-PrOH	6.255	2.730	2.839, 3.7[c)]

a)b) See footnotes a and b of Table 1. c) Ref. 12c. d) D=dioxane.

sion for the solvolyses of all the β-arylalkyl tosylates, **1** and **3** (Entries 1—8 in Table 3, Figs. 2, 3, 4, and 5). The deviation from linearity in aqueous TFE mixtures, EtOH–TFE mixtures, and acetic and formic acids, are inconsistent with what would have been expected for nucleophilic solvent assistance. The dispersion pattern in correlations with Eq. 1 is essentially the same for all of the tosylates (**1** and **3**) having more electron-donating substituents than the parent compound, and is characteristic of aryl-assisted systems. The application of Eq. 1 using the Y_{OTs} scale gave poor correlations for the typical aryl-assisted solvolyses of Entries 1—5 in Table 3 (R=0.95—0.97; SD=±0.16—0.25). In contrast, there is a better fit to Y_{OTs} for arylcycloalkyl-OTs **3** having electron-attracting substituents and for **4** and neopentyl-OTs **5** (Entries 8—13 and Figs. 5, 6, 7, and 8). When plotted against the 2-adamantyl k_c standard, the correlations (Table 3) show m values <1, suggesting that all of the substrates react by the k_Δ pathway.

Not surprisingly, the application of Eq. 2, which adds a term for the solvent nucleophilicity, does not effectively improve the correlations, since all of the compounds have a neopentyl-type structure. In fact, for Entries 1—8 a significantly negative value of the solvent nucleophilicity term (l) is obtained, which is difficult to explain unless it results from an artifact. In contrast, the parent cyclopropylmethyl tosylate **6** correlates with Eq. 2 and displays a significant extent of nucleophilic solvent assistance (l=0.31; Entry 14 in Table 3).

When Eq. 5, which uses the Y_Δ, instead of Y_{OTs}, scale, is applied, significantly better correlations (R>0.994; SD<0.09) are observed only for solvolyses of three β-arylalkyl tosylates (Entries 2—4). The correlations for all other tosylates are less satisfactory, as shown by the $R<0.97$ and SD>0.20 values (Table 4). A significant difference in the goodness of fit of the correlations between the solvolyses of these two groups of substrates is apparent.

The strong aryl-assistance in the solvolysis of [1-(*p*-methoxyphenyl)cyclobutyl]methyl tosylate (**3A**) leads to a better correlation with the Y_Δ scale. The preference for correlation with this scale decreases for the *p*-methyl derivative (**3M**); this scale is distinctly less preferable ($R<0.95$) for the correlation of the unsubstituted derivative (**3H**) (Figs. 3, 4, and 5). This is in sharp contrast to the excellent linear correlation of **3H** vs. Y_{OTs} with $R>0.99$ and SD<0.09 of acceptable conformity. The same is true for the electron-withdrawing *p*-chloro (**3C**) (Fig. 6) and *m*-bromo (**3B′**) substituted system. The Y_Δ scale also gives extensive dispersion for correlations of [1-(*p*-methoxyphenyl)cyclopropyl]methyl tosylate (**4A**) and (1-phenylcyclopropyl)methyl] (**4H**), whereas the Y_{OTs} scale gives better correlations (Figs. 7 and 8). A comparison of the correlations with Eq. 1 vs. those with Eq. 5 for these solvolyses enables a reasonable distinction between the k_c and k_Δ mechanisms, and indicates a gradual change in conformity to the two extreme Y parameters, Y_{OTs} and Y_Δ.

Schleyer and co-workers had noted that the solvolysis rates of **2**, i.e., Y_{OTs}, correlated linearly with those for **1A** in solvents where data were available, and also with those for the unsubstituted neophyl tosylate (**1H**) in typical solvolyzing solvents, including ethanol and trifluoroacetic acid.[5)] Roberts reported a linear relationship between the $\log k$ values for **1H**–OTs and **2**–OTs for aqueous ethanol and acetic acid–formic acid mixtures.[7)] Their results which were based on limited solvent sets, are in contrast to ours more extensive data sets shown by Fig. 2. In addition, solvolyses (Entries 4—8) in more extended series of solvents result in an even better fits to Eq. 5 when $\log k$ values of **1H**, rather than the *p*-methoxyneophyl-based Y_Δ scale, are used, indicating a gradual change in the best-fit Y scale describing the respective solvolyses.

Analysis of Anchimeric Assistance Pathways. The present set of β-arylalkyl solvolyses can be successfully analyzed by a linear combination of Y_{OTs} and Y_Δ i.e., by Eq. 3. The extremely high precision ($R>0.995$ and SD<0.09) shown in Table 5 and demonstrated in Figs. 9 and 10 is in sharp contrast to those in Figs. 4 and 5.

The m_c and m_Δ values change widely with the nature of the substrate in a complementary way (Table 5): m_c increases

Table 3. Correlation Analysis of Solvent Effects on Solvolyses of Aralkyl Tosylates According to Eq. 2: $\log(k/k_{80E}) = mY_{OTs} + lN_{OTs}$

No.	R in ROTs	°C	m	l	n	R	±SD
1.	*p*-Methoxyneophyl	45	0.50		49	0.953	0.23
			0.47	−0.15		0.969	0.19
2.	[1-(*p*-Methoxyphenyl)cyclobutyl]methyl	45	0.52		35	0.955	0.22
			0.46	−0.13		0.971	0.18
3.	Neophyl	45	0.68		46	0.968	0.25
			0.60	−0.16		0.983	0.19
4.	[1-(3,4-Dimethylphenyl)cyclobutyl]methyl	45	0.61		33	0.963	0.23
			0.53	−0.19		0.983	0.16
5.	[1-(*p*-Methylphenyl)cyclobutyl]methyl	45	0.60		32	0.979	0.17
			0.55	−0.13		0.988	0.12
6.	[1-(*m*-Methylphenyl)cyclobutyl]methyl	45	0.59		31	0.990	0.11
			0.56	−0.08		0.994	0.08
7.	[1-(3-Bromo-4-methoxyphenyl)cyclobutyl]methyl	45	0.51		31	0.984	0.12
			0.48	−0.07		0.988	0.10
8.	(1-Phenylcyclobutyl)methyl	45	0.62		30	0.996	0.07
			0.60	−0.02		0.996	0.07
9.	[1-(*p*-Chlorophenyl)cyclobutyl]methyl	45	0.58		24	0.989	0.08
			0.60	0.05		0.993	0.07
10.	[1-(*m*-Bromophenyl)cyclobutyl]methyl	45	0.57		11	0.989	0.07
			0.61	0.03		0.991	0.06
11.	[1-(*p*-Methoxyphenyl)cyclopropyl]methyl	25	0.64		31	0.995	0.08
			0.66	0.07		0.997	0.07
12.	(1-Phenylcyclopropyl)methyl	25	0.68		26	0.995	0.09
			0.70	0.07		0.996	0.08
13.	Neopentyl	45	0.62		13	0.997	0.09
			0.63	0.02		0.997	0.09
14.	Cyclopropylmethyl	25	0.70		18	0.956	0.26
			0.85	0.31		0.991	0.13
15.	2-Adamanthyl	25	1.00	0.00	(Definition)		

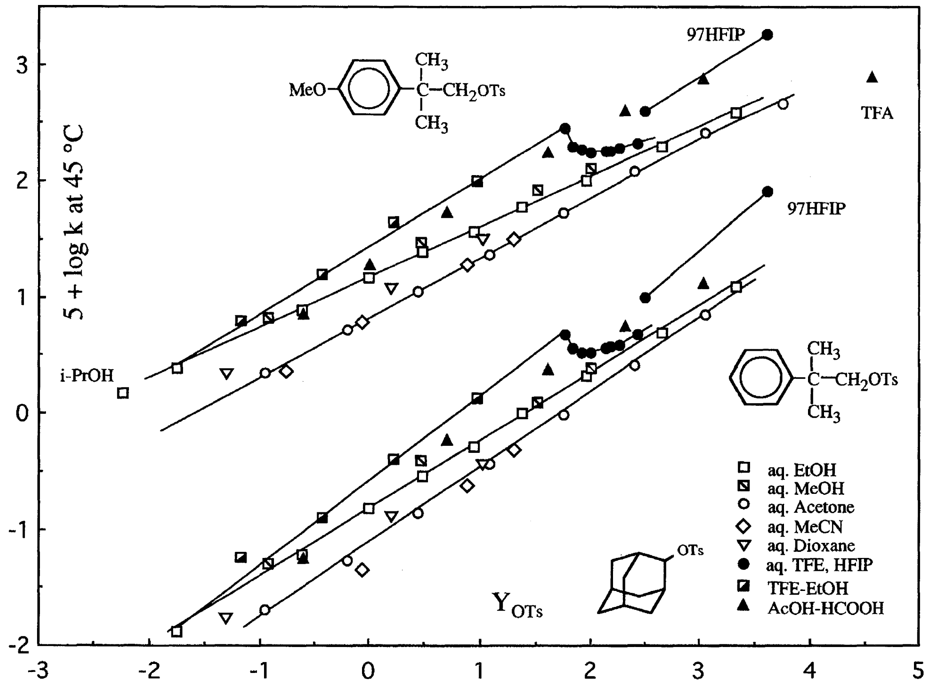


Fig. 2. The mY_{OTs} plots of solvent effect for the solvolyses of neophyl tosylates **1**.

from 0.00 for the mechanistic extreme represented by **1A** solvolysis (Entry 1) to 1.00 for **2**-OTs (Entry 15) at the other extreme, whereas m_Δ decreases in parallel for the same substrates and substituents. In order to adequately evaluate the

Table 4. Correlation Analysis of Solvent Effects of Solvolyses of Aralkyl Tosylates According to Eq. 5:[a] $\log(k/k_{80E})=m'Y_{\Delta}+lN_{OTs}$

No.	R in ROTs	°C	m'	l	R	±SD
1.	*p*-Methoxyneophyl	45	1.00		(Definition)	
2.	[1-(*p*-Methoxyphenyl)cyclobutyl]methyl	45	0.99		0.999	0.03
			1.00	0.01	0.999	0.03
3.	Neophyl	45	1.23		0.995	0.09
			1.27	0.05	0.996	0.08
4.	[1-(3,4-Dimethylphenyl)cyclobutyl]methyl	45	1.16		0.994	0.09
			1.13	−0.02	0.994	0.09
5.	[1-(*p*-Methylphenyl)cyclobutyl]methyl	45	1.14		0.987	0.13
			1.17	0.04	0.988	0.13
6.	[1-(*m*-Methylphenyl)cyclobutyl]methyl	45	1.11		0.970	0.18
			1.20	0.09	0.975	0.17
7.	[1-(3-Bromo-4-methoxyphenyl)cyclobutyl]methyl	45	0.98		0.976	0.14
			1.06	0.08	0.981	0.13
8.	(1-Phenylcyclobutyl)methyl	45	1.06		0.951	0.23
			1.22	0.14	0.962	0.20
9.	[1-(4-Chlorophenyl)cyclobutyl]methyl	45	0.86		0.885	0.26
			1.15	0.20	0.933	0.20
10.	[1-(*m*-Bromophenyl)cyclobutyl]methyl	45	0.72		0.891	0.21
			1.11	0.18	0.939	0.17
11.	[1-(*p*-Methoxyphenyl)cyclopropyl]methyl	25	1.19		0.940	0.29
			1.36	0.26	0.962	0.24
12.	(1-Phenylcyclopropyl)methyl	25	1.24		0.946	0.29
			1.40	0.22	0.961	0.25
13.	Neopentyl	45	1.16		0.984	0.16
			1.27	0.12	0.993	0.12
14.	Cyclopropylmethyl	25	1.09		0.828	0.50
			1.50	0.38	0.875	0.45
15.	2-Adamantyl	25	1.82		0.953	0.45
			1.97	0.25	0.964	0.40

a) $Y_{\Delta}=\log(k/k_{80E})_{\mathbf{1A}}$.

Table 5. Correlation Analysis of Solvent Effects of Solvolyses of Aralkyl Tosylates According to Eq. 3: $\log(k/k_{80E})=m_cY_{OTs}+m_{\Delta}Y_{\Delta}$

No.	R in ROTs	m_c	m_{Δ}	R	±SD	$\underline{m}$[a]	M_{Δ}[b]
1.	*p*-Methoxyneophyl	0.00	1.00			0.51	1.00
2.	[1-(*p*-Methoxyphenyl)cyclobutyl]methyl	0.06	0.89	0.9995	0.02	0.51	0.88
3.	Neophyl	0.16	0.95	0.998	0.06	0.64	0.75
4.	[1-(3,4-Dimethylphenyl)cyclobutyl]methyl	0.15	0.90	0.997	0.07	0.61	0.75
5.	[1-(*p*-Methylphenyl)cyclobutyl]methyl	0.27	0.67	0.999	0.04	0.61	0.56
6.	[1-(*m*-Methylphenyl)cyclobutyl]methyl	0.39	0.41	0.999	0.04	0.60	0.35
7.	[1-(3-Bromo-4-methoxyphenyl)cyclobutyl]methyl	0.29	0.45	0.997	0.06	0.52	0.44
8.	(1-Phenylcyclobutyl)methyl	0.50	0.22	0.998	0.04	0.61	0.18
9.	[1-(*p*-Chlorophenyl)cyclobutyl]methyl	0.59	−0.03	0.989	0.08	0.57	−0.03
10.	[1-(*m*-Bromophenyl)cyclobutyl]methyl	0.60	−0.06	0.989	0.07	0.57	−0.05
11.	[1-(*p*-Methoxyphenyl)cyclopropyl]methyl	0.60	0.08	0.995	0.08	0.65	0.06
12.	(1-Phenylcyclopropyl)methyl	0.63	0.10	0.995	0.09	0.68	0.07
13.	Neopentyl	0.54	0.18	0.996	0.09	0.63	0.15
14.	Cyclopropylmethyl	1.10	−0.79	0.977	0.20		
15.	2-Adamantyl	1.00	0.00			1.00	0.00

a) $\underline{m}=m_c+0.51m_{\Delta}$. b) $M_{\Delta}=0.51m_{\Delta}/(m_c+0.51m_{\Delta})$.

degree of similarity to both reference models **1A** and **2**, it is necessary to normalize the m scales for the different intrinsic susceptibilities of both reference Y scales, Y_{Δ} and Y_{OTs}. Thus, we define the measure $\underline{m}$ of the response to the solvent ionizing power (or the solvent polarity) for a given substrate by $\underline{m}=m_c+\alpha m_{\Delta}$, where α is a normalizing factor for the m_{Δ} scale. The value $\alpha=0.51$ appears to be the most suitable for a wide range of relevant solvolyses.[15] This normalization leads to reasonable apparent responses ($\underline{m}$-values) of a given substrate to the solvent polarity, which reflect the extent of positive charge developed at the reaction center in the transition state. The blending parameter of the response

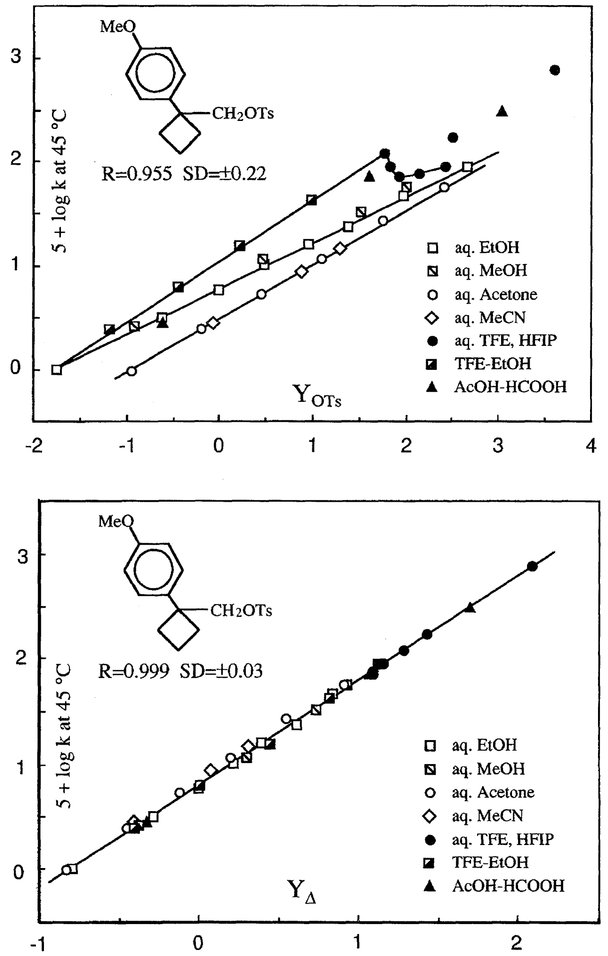


Fig. 3. The mY_{OTs} and $m'Y_{\Delta}$ plots of solvent effect for the solvolysis of [1-(*p*-methoxyphenyl)cyclobutyl]methyl tosylate **3A** at 45 °C.

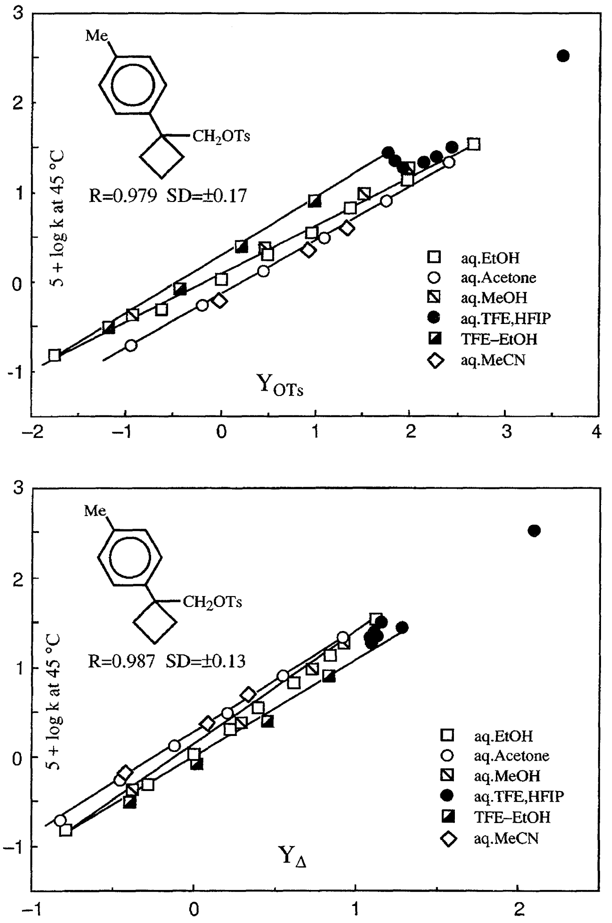


Fig. 4. The mY_{OTs} and $m'Y_{\Delta}$ plots of solvent effect for the solvolysis of [1-(*p*-methylphenyl)cyclobutyl]methyl tosylate **3M** at 45 °C.

to the Y_{Δ}vs. Y_{OTs} scale, $M_{\Delta}=\alpha m_{\Delta}/\underline{m}$ or $=\alpha m_{\Delta}/(m_c+\alpha m_{\Delta})$, varies consistently and monotonically within the range from 0.00 for **2** to 1.0 for **1A** as shown in Table 5. This is in the direction expected if the dispersion in the Y_{OTs} plot becomes more pronounced as anchimeric assistance becomes more significant. There seems to be a continuous spectrum of the degree of dispersion in correlations involving solvent effects of anchimerically assisted solvolyses between the k_c and k_{Δ} mechanistic extremes, i.e., a continuous spectrum of aryl-assisted k_{Δ} solvolyses involving varying degrees of neighboring group assistance. This contrasts sharply with the suggestions that only a correlation with either Eq. 1 or Eq. 5 provides a clear-cut method of distinction between bridged k_{Δ} or open k_c categories of solvolysis.

The excellent linear free-energy correlation with Eq. 3 may serve as evidence that the reaction proceeds by a single mechanism in the solvents examined. It is however often pointed out that the use of a dual-parameter analysis, with an increased number of parameters, has a general tendency to correlate almost any data moderately successfully. Consequently, the confidence in assigning a single solvolytic process in the absence of a competing route relies heavily upon the precision level of the fit of the correlation. The criterion of acceptable conformity of the correlations which we apply in the present analysis, i.e., SD$<$0.09 and $R>0.995$, is extraordinarily high compared with the ordinary precision of fit observed in correlations given in the literature.[5)]

From this viewpoint, the correlations for the *p*-chloro and *m*-bromo derivatives of **3**, with Eq. 3 (Entries 9 and 10 in Table 5) were poor, as compared with other electron-donating substituent sets, whereas the correlation with Y_{OTs} involving a lN component ($l\fallingdotseq 0.05$) gave a better fit (Entries 9 and 10 in Table 3). However, it is reasonable to assume that M_{Δ} is practically zero ($m_{\Delta}=0$) for these deactivated derivatives.

Discussion

Substituent Effects. The substituent effects on the neophyl solvolysis have been reported earlier for a sufficient set of substituted neophyl brosylates in acetic acid,[16)] and for the *m*-nitrobenzenesulfonates in several solvents.[17)] In all of the solvents, regardless of the sulfonate leaving group, we obtained excellent Yukawa–Tsuno correlations (Eq. 4) with an identical *r* value of 0.57, which is characteristic of aryl-assisted solvolyses. The solvolysis of threo-2-aryl-1-methylpropyl brosylates gave a nonlinear correlation for Eq. 4, but again r=0.56 for the k_{Δ} pathways.[18)] This was ascribed to competition with a k_s process for systems carrying electron-

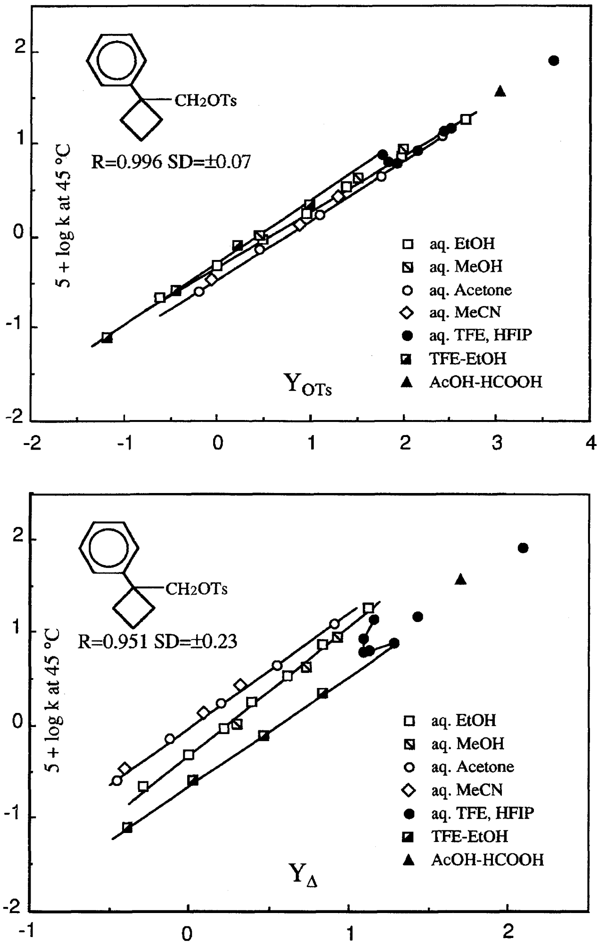


Fig. 5. The mY_{OTs} and $m'Y_{\Delta}$ plots of solvent effect for the solvolysis of 1-(*p*-phenylcyclobutyl)methyl tosylate **3H** at 45 °C.

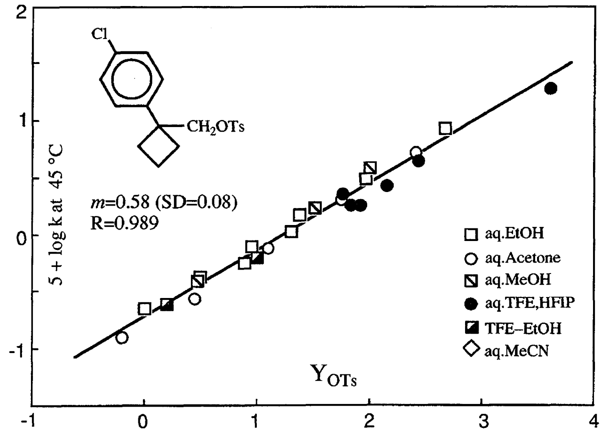


Fig. 6. The mY_{OTs} plots of solvent effect for the solvolysis of [1-(*p*-chlorophenyl)cyclobutyl]methyl tosylate **3C** at 45 °C.

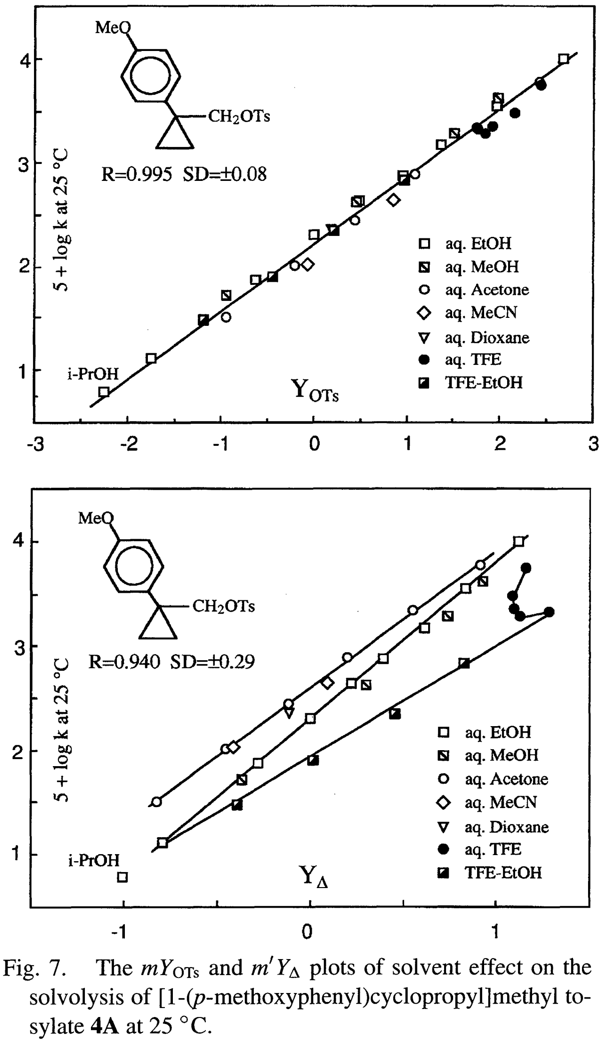


Fig. 7. The mY_{OTs} and $m'Y_{\Delta}$ plots of solvent effect on the solvolysis of [1-(*p*-methoxyphenyl)cyclopropyl]methyl tosylate **4A** at 25 °C.

withdrawing substituents, and confirmed by the concomitant formation of the erythro isomer.[19] For the solvolysis of (1-arylcyclobutyl)methyl tosylates **3**, one may expect a linear correlation with the most appropriate $\overline{\sigma}_{\Delta}$ value (apparent σ value at r=0.57 in Eq. 4) based on the neophyl solvolysis, due to the very close structural similarity of systems **1** and **3**. However, the solvolysis of **3** gives a concave plot against $\overline{\sigma}_{\Delta}$, similar to that observed for the solvolysis of *threo*-2-aryl-1-methylpropyl brosylates. This indicates a mechanistic changeover as the substituent changes. If we assume a competition of aryl-assisted and unassisted pathways, we can correlate the overall substituent effect by the respective Yukawa–Tsuno Equations for both pathways.[20] The results for the acetolysis are plotted in Fig. 1.

From this plot for the overall substituent effect, systems substituted by a *p*-methoxy group, such as **3A**, or by more electron donating groups should react by the k_{Δ} mechanism, whereas the solvolysis of the 3,4-dimethyl (**3MM′**), the *p*-methyl **3M**, the *m*-methyl (**3M′**), or the 3-bromo-4-methoxy (**3AB′**) derivatives should involve an increasing amount of competing unassisted process in this order. The unsubstituted derivative **3H** should predominantly react via the aryl-unassisted process and the *p*-chloro **3C** and the *m*-bromo **3B′** derivatives react exclusively by this route. This mechanistic changeover with the substituents should also be reflected in the solvent effect on the solvolysis of these derivatives.

Solvent Effect Analysis and Mechanistic Assignment. The correlation with Eq. 3 has revealed that a blend of solvent

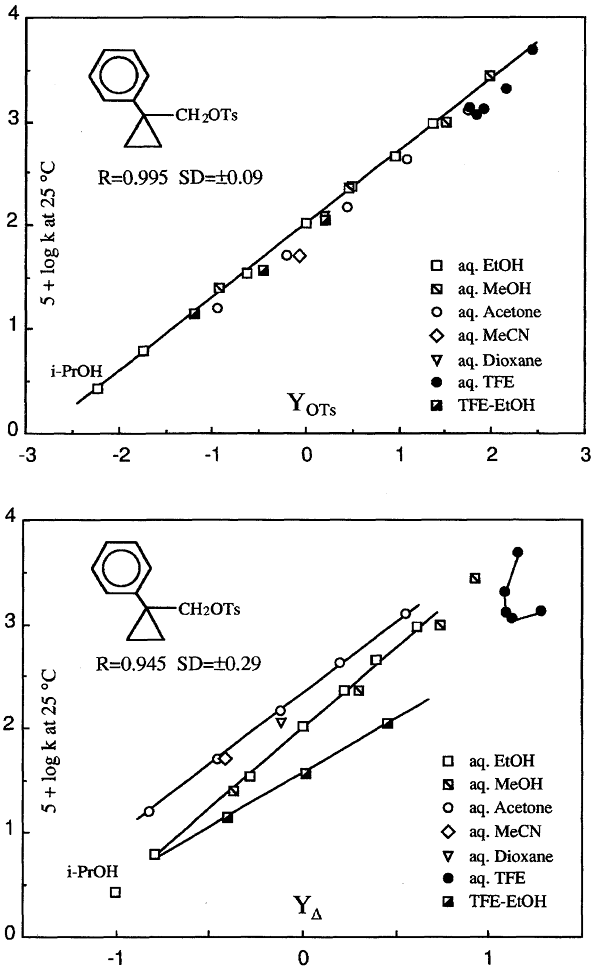


Fig. 8. The mY_{OTs} and $m'Y_\Delta$ plots of solvent effect on the solvolysis of 1-(*p*-phenylcyclopropyl)methyl tosylate **4H** at 25 °C.

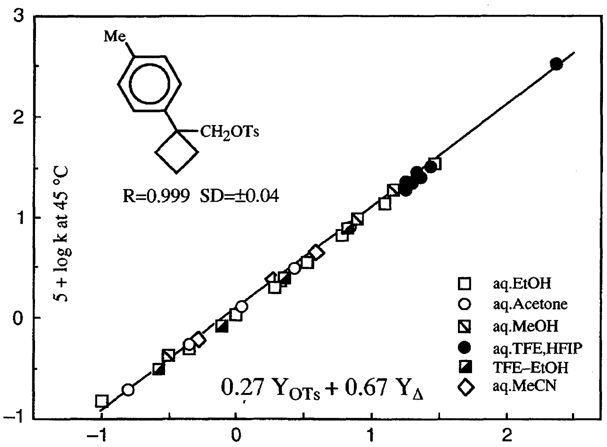


Fig. 9. The (m_cY_{OTs}+$m_\Delta Y_\Delta$) plots for the solvolysis of [(1-*p*-methylphenyl)cyclobutyl]methyl tosylate **3M** at 45 °C.

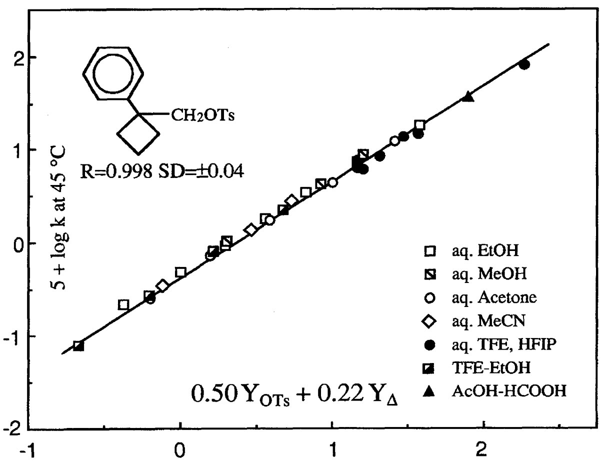
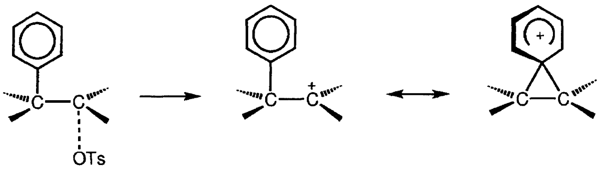


Fig. 10. The (m_cY_{OTs}+$m_\Delta Y_\Delta$) plots for the solvolysis of (1-phenylcyclobutyl)methyl tosylate **3H** at 45 °C.

polarity scales (Y_Δ and Y_{OTs}) correlates with a wide range of β-arylalkyl solvolyses involving neighboring group assistance. The k_Δ solvolyses can be successfully correlated with Eq. 3 with extremely high precision: R>0.995 and SD<0.09 with m_c and m_Δ values which vary with the substrate and the substituent. The blending parameter (M_Δ) also varies monotonically from 1.0 for the k_Δ reference **1A**, via intermediate values for **1H**, **3MM′**, **3AB′**, **3M**, and **3M′**, to a value close to zero for **4**, and to 0 for **3C** and **3B′**, and the k_c reference compound **2**. M_Δ decreases monotonically with a decrease in the electron-donating ability of the substituents within substrates **1** and **3**, and measures the extent of anchimeric assistance in the transition state.

Anchimerically assisted solvolyses of β-arylalkyl precursors (**7**) proceed through the first formed intermediate, which is represented in Fig. 11 as a hybrid of hypothetical canonical structures of the open ion (**8**) and the bridged (phenonium) ion (**9**). In aryl-assisted systems, a large extent of the incipient cationic charge is transferred to the assisting aryl moiety as the contribution of the bridged form **9** in the transition state increases. In the ordinary k_Δ process, ionization and migration occur synchronously in the rate-determining step leading to **9**, whereas in a k_c process the neighboring group may migrate to the cationic site of **8** after the rate-determining ionization. Both of these extremes may be characterized by the geometry, i.e., by the aryl–α-carbon distance in the transition state.

For the solvolysis of the (1-arylcyclobutyl)methyl tosylate series **3**, the nonlinear substituent effect in Fig. 1 suggests a gradual change from the aryl-assisted mechanism for the electron-donating substituents to the aryl-unassisted mechanism for the electron-withdrawing ones. The large m_Δ



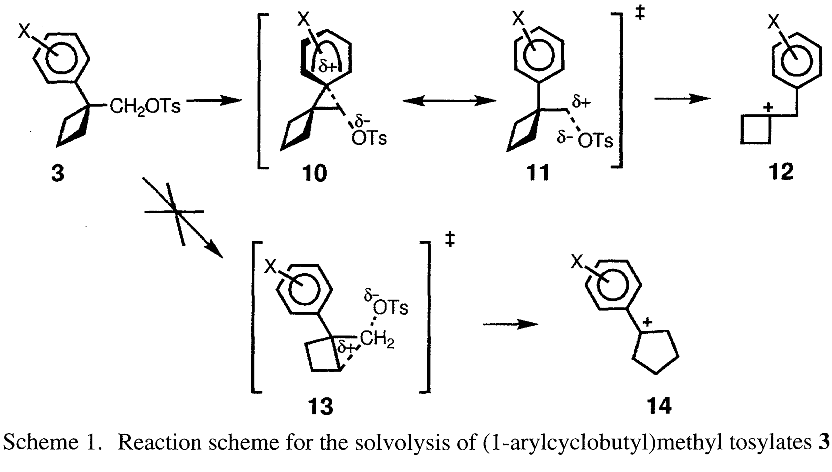
7 8 9

Fig. 11. Canonical form (**8**, **9**) of the intermediate for k_Δ solvolysis of **7**.

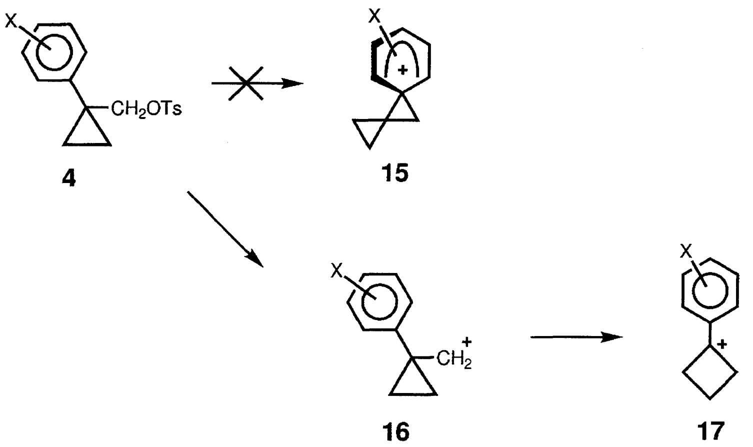
value for the *p*-methoxy derivative **3A** indicates a strong aryl-assistance at the transition state, whose extent gradually decreases via the 3,4-dimethyl derivative **3MM′** to the *p*-methyl derivative **3M**. For simplicity, the structures of transition states are approximated by those of the corresponding intermediates. From the M_Δ value, the transition state for **3A** may be modeled by structure **9**, those for **3MM′**, **3M**, **3AB′**, and **3M′** best modeled by a hybrid of **8** and **9**, and those for **3H**, **3C**, and **3B′** are essentially described by the open cation structure **8**. The latter should also represent the intermediate in the solvolysis of more electron-withdrawing derivatives. Nucleophilic solvent participation is not considered for these neopentyl-like derivatives. In fact, the solvolysis of **3**, irrespective of the substituents, gives only aryl-rearranged products. Products derived by the alkyl-assisted or the solvent assisted (k_s) pathways are absent, even for derivatives bearing strongly electron-withdrawing substituents, such as *p*-nitro.[10,11] Hence, all of the substituted derivatives solvolyze by the aryl-assisted pathway involving widely different degrees of assistance. For electron-withdrawing derivatives, although the solvolysis still belongs to the same mechanistic category, the charge delocalization in the transition state is much lower. The substituent effect analysis indicates that the substituent change causes a clear mechanistic change from aryl-assisted (k_Δ) to aryl-unassisted (k_c) mechanism, but it is ambiguous whether the two mechanisms proceed exclusively or competitively. It is therefore remarkable that Eq. 3 applies with a uniform equal precision to **3M**–**3H** and **3C** with m_Δ values in the 1.00—0.0 range. This leads to the conclusion that the reaction proceeds by a single mechanism rather than by competition of aryl-assisted and aryl-unassisted routes. The M_Δ value varies monotonically with the substituents from 0.88 for *p*-MeO to 0.0 for *m*-Br, showing a decreased dispersion of the Y_{OTs} plot for decreasing anchimeric assistance. All compounds **3** must solvolyze through the aryl-assisted pathway involving widely differing degrees of assistance, ranging from the bridged ion (**10**) for *p*-MeO to the open ion k_c (**11**) for *m*-Br, as illustrated in Scheme 1. A substituent-effect analysis suggests a gradual shift of the transition state structure from **10** to **11** for electron-withdrawing substituents all within the same mechanism. A correlation analysis for solvent change using the dual-parameter Eq. 3 is compatible with all of the mechanistic probes. It is noteworthy that no reaction course leading to the cyclopentyl derivative (**14**) via alkyl assistance of the cyclobutyl ring [transition state (**13**)] was found.

In contrast, (1-arylcyclopropyl)methyl tosylates **4A** and **4H** behave as simple k_c-substrates according to the substituent effect analysis.[10] In the solvent-effect analysis, these solvolysis rates show complete linearity against Y_{OTs}, i.e., $m_\Delta \doteqdot 0.1$, and, hence, the reaction proceeds through the aryl-unassisted pathway regardless of the aryl substituent. This mechanistic assignment was also corroborated by the product analysis which revealed the exclusive formation of phenylcyclobutyl derivatives.[10,12] The lack of aryl-assistance may be due to the high stabilization of the transition state by the cyclopropylmethyl–cyclobutonium ion resonance[12] and to the highly strained spiro[2.2]pentane structure (**15**) in the transition state of the aryl-bridging pathway (Scheme 2). Furthermore, the cyclopropyl-assisted pathway must also be considerably enhanced by the aryl-resonance stabilization of the charge developed at the benzylic position in the transition state for ring-expansion (**17**). This may be the reason for the low M_Δ value in the solvolysis of **4**. Unanswered questions are how effective is the alkyl-assistance and whether alkyl migration is concomitant with or subsequent to ionization. While the precise nature or structure of the cationic intermediate (**16**) derived from compounds **4** is controversial,[12,21] our work indicates that charge delocalization in the carbocation-like transition state derived from **4** resembles **3C** and **3B′** in not involving aryl-bridging. The solvolyses of **4A** and **4H** are essentially correlated with Y_{OTs} without any contribution of Y_Δ.

Solvolysis of the parent cyclopropylmethyl tosylate **6** is remarkably accelerated by anchimeric assistance in all of the solvents.[22] Nevertheless, there is no delocalization-induced dispersion, giving an m=0.85 and an appreciable sensitivity to solvent nucleophilicity of l=0.31 (Entry 14 in Table 3). This implies an insignificant intramolecular charge delocalization within the transition state. An appreciable solvent nucleophilic assistance, arising not from the k_s contribution but from the nucleophilicity-dependent product-forming process



Scheme 1. Reaction scheme for the solvolysis of (1-arylcyclobutyl)methyl tosylates **3**.



Scheme 2. Reaction scheme for the solvolysis of (1-arylcyclopropyl)methyl tosylates **4**.

involving the ion-pair partition into very inactive cyclobutyl tosylate is possible.[12c,22] Hence, there is a significant difference in both the dispersion behavior and the solvent stabilization between aryl-bridged and alkyl-assisted (including hyperconjugative) transition states.

Equation 3 may be rewritten in the form of Eq. 7,[8]

$$\log(k/k_{80E}) = \underline{m}[Y_{OTs} + M_{\Delta}(\underline{Y}_{\Delta} - Y_{OTs})], \tag{7}$$

where $\underline{Y}_{\Delta}$ is the ionizing power scale for the delocalized transition state referred to the normalized Y_{Δ} scale by a factor of 1/0.51.[15] The susceptibility parameter $\underline{m}$ corresponds to $m_c+0.51m_{\Delta}$ and $M_{\Delta}=0.51m_{\Delta}/(m_c+0.51m_{\Delta})$ in Eq. 7. On introducing the dual similarity comparison treatment of Eq. 3, we used the same framework of charge-localization (Y_{OTs}) and delocalization ($\underline{Y}_{\Delta}-Y_{OTs}$) components by the solvent as in the Yukawa–Tsuno framework for the substituent effect.[9] The M_{Δ} term may be closely related to the resonance term in the Yukawa–Tsuno Equation (Eq. 4). Since the M_{Δ} parameter should be related more intimately to the total extent of the delocalization, its main components are the delocalization effect of the parent phenyl group with the reaction center and the resonance effect of the π-donor substituent. At least, it is apparent that M_{Δ} should be zero for a system of $r=0$. It is noteworthy that the dependence of M_{Δ} upon substituents differs significantly from system to system; M_{Δ} values for the pairs of *p*-MeO and *p*-H substrates are 1.00; 0.75 for **1**, 0.88; 0.18 for **3** and 0.78; 0.32[23] for *threo*-2-aryl-1-methylpropyl tosylates. Clearly, whereas the delocalization effect of the parent phenyl group is important for the solvolysis of **1** and less important for **3**, the importance of the resonance effect by the π-donor ($\Delta\overline{\sigma}_{R}^{+}$ term) is in the reverse order. In contrast, the $\underline{m}$ value is generally much less sensitive to a change in the substituents, being 0.5—0.7 for all of the present systems, as shown in Table 5. We believe that $\underline{m}$ should serve as a reasonable measure of the cationic nature of the transition state.

One may anticipate that Eq. 7 will be applicable not only to anchimerically aryl-assisted solvolyses, but also to other solvolyses involving different charge-delocalization mechanisms. Indeed, we have found several good correlations with Eq. 7, e.g., of benzylic tosylates solvolyses proceeded by the nucleophilically limiting mechanism.[8] Tris(*p*-methoxyphenyl)vinyl tosylate shows an extremely high M_{Δ} value of 1.54, indicating highly enhanced delocalization by the *α*-*p*-methoxyphenyl group in forming the transition state.[8,24] Except for this vinylic system and our recent solvent effect studies in benzylic systems showing enhanced charge delocalization,[8] we know of no good examples of solvolyzing benzylic tosylate systems involving significant charge delocalization in the transition state. Before further development of Eq. 7 and defining new parameters, such as $\underline{Y}_{\Delta}$ or ($\underline{Y}_{\Delta}-Y_{OTs}$), more solvolysis data of systems showing an enhanced resonance effect in a sufficient number of solvents are required.

The Continuous Spectrum of k_c–k_{Δ} Mechanisms. The dispersion measured by the M_{Δ} value becomes more significant with the increased degree of aryl-assistance, which is accompanied by enhanced charge delocalization in the transition state.

The present (1-arylcycloalkyl)methyl series supply an experimental manifestation of the varying extent of anchimeric assistance by the neighboring groups. Solvolysis reactions span a wide range of anchimeric assistance, from completely synchronous assistance process (for **1A** and **3A**), via moderately to weakly assisted process (for **1H**, **3MM′**, **3M**, **3AB′**, **3M′**, and **3H**), to completely unassisted limiting k_c process (for **3C**, **3B′**, **4A**, and **4H**). This wide scope of the k_{Δ} process may be regarded as representing a continuous "spectrum", implying a progressive change in the transition-state character. The M_{Δ} value is a proper tool of monitoring the varying extent of aryl-bridging at the transition state of anchimerically assisted solvolyses. For a strongly assisted solvolysis there is a high contribution of hybrid **9**, while in moderately aryl-assisted systems the transition state is a resonance hybrid of **8** and **9**. Furthermore, simple ionization to an open carbocation is accompanied by only a small change in the C_{Ar}–C_{α} distance. The charge is delocalized in a transition state-like **8** by an enhanced hyperconjugative interaction between the incipient carbocation 2p-orbital and the available *β*-bonding orbitals.

The unassisted extreme in the mechanistic spectrum is modeled by an open cationic intermediate stabilized by an enhanced hyperconjugative 2p(C^+)-β-bonding orbitals interaction. This may cause the significantly reduced m values of 0.6—0.7 for systems **3C**, **3B′**, and **4**. Roberts had pointed out the characteristic different response to the solvent by a substrate ionizing with neighboring-group assistance compared with one ionizing with "assistance" by exalted hyperconjugation.[7)]

It should be noted that the m_Δ value for the neopentyl tosylate **5** is appreciable compared with the values found for compounds **4**. This may reflect the involvement of a significant degree of neighboring alkyl-group assistance. σ-Alkyl bridging will also delocalize the cationic charge between the α- and β-positions, but in spite of this no significant solvent effect was found on the ionization rates of most aliphatic precursors. The effect of alkyl-assistance as measured by the M_Δ value is found to be extremely small and difficult to unequivocally corroborate, in contrast with those found for aryl-assisted substrates. A similar situation holds for other well known examples, such as pinacolyl(1,2,2-trimethylpropyl), 1-(1-adamantyl)ethyl (M_Δ=0.20),[1)] and 2-*exo*-norbornyl where the solvolysis mechanism and particularly the question whether alkyl migration is concomitant with or subsequent to ionization are still controversial.[25)] We believe that for the concerted ionization-migration case, the m_Δ parameter must be less susceptible to the charge delocalization on the alkyl skeleton in the alkyl-assisted transition state than in the extensive delocalization for an aryl-bridged transition state. The delocalization-induced dispersion in the $Y_{\rm OTs}$ plot can be virtually regarded as being characteristic of the aryl-assisted process. In the case of the two-step mechanism the solvent may affect the rate-determining transition state in a way similar to that in which the transition state for the formation of a localized cation, such as 2-adamantyl, is affected. A serious question then arises as to whether the solvolyses of substrates with an apparent m_c or $(m_c+0.51m_\Delta)<0.8$ are no longer good models for k_c processes where the charge is not *delocalized*.[5,26)] Therefore, mechanistic assignments based on an analysis of the solvent effect are still appreciably less clear-cut in cases when the dispersion behavior is less significant. This is also the case for **4** and the electron-withdrawing substituent series of **3** with low M_Δ value and reduced m value.

Finally, we should point out the particular importance of charge delocalization as a cause of the characteristic dispersion in the correlations of solvent effects. The origin of the wide-scope "dispersion" phenomenon has so far been attributed to differences in the solvation of the transition states of aromatic and aliphatic derivatives.[1,2a,2c,2d,2e,6,8,13,24,27)] It is therefore remarkable that solvolysis of all the (1-arylcyclopropyl)methyl tosylates **4** does not show any characteristics of the anchimeric aryl-assisted k_Δ process even for the strong π-electron-donative *p*-methoxy derivative. Consequently, the dispersion behavior of aryl derivatives must arise from a direct involvement of the aryl π-system in the delocalization of the carbocation charge in the transition state. The unassisting aryl group in the transition state of a k_c process *does not* cause any significant dispersion in the $Y_{\rm OTs}$ plot. An extraneous solvation effect of an insulated nonconjugative aromatic ring does not contribute to the dispersion behavior.

In the present study we have shown that Eq. 3 correlates with high precision to the solvent effects on anchimerically assisted solvolyses, and is therefore capable of serving as a diagnostic probe of the aryl-assisted solvolysis mechanism. An analysis by Eq. 3 of a wider range of neighboring group assisted solvolyses and also of benzylic k_c solvolyses, which have a different mechanism of charge delocalization, will be given in a forthcoming paper.

Experimental

Materials: (1-Arylcycloalkyl)methanols were prepared by the method reported by Roberts.[11,12)] (1-Arylcyclobutyl)methanols were prepared by a reaction of the arylacetonitriles and 1,3-dibromopropane with sodium hydride in DMSO, followed by alkaline hydrolysis of the formed cyclic nitriles in diethylene glycol and then by a $LiAlH_4$ reduction of the obtained acid or acid chloride.[11b)] (1-Arylcyclopropyl)methanols were prepared in a similar way, except that in the first stage the arylacetonitrile and 1,2-dibromoethane reacted with sodium amide in ether.[12d)]

The tosylates were prepared by the Tipson procedure[28)] from the corresponding alcohol and *p*-toluenesulfonyl chloride in pyridine, and were recrystallized from the appropriate solvent. Their physical properties and elemental analysis are given in Table 6.

Binary solvent mixtures were prepared by mixing the corresponding volumes or weights of the pure solvents at 25 °C, as described before.[1,6,13)]

Kinetic Measurements: Solvolyses in binary aqueous organic mixtures were followed conductimetrically, as described earlier.[1,6,13)] Using a conductivity meter (CM-50AT and CM-60S equipped with an interval time unit and printer, Toa Electronics Ltd.), solvolyses were followed in a thermostatted bath controlled to ±0.01 °C by taking at least 100 readings at appropriate intervals during 3 half-lives, and an infinity reading after 10 half-lives. The experimental errors in respective runs were generally <1.0% and the reproducibility of the rate constants was ≦1.5%.

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

Table 6. Physical Constants of Aralkyl Tosylates

ROTs	Mp/°C (Lit, mp/°C)	Carbon/%		Hydrogen/%	
		Found	Calcd	Found	Calcd
3H	96.5—97.5 (97—98)[a)]	68.17	68.31	6.35	6.37
3MM′	101.0—101.5	69.77	69.74	6.98	7.02
3M	82—82.9	68.87	69.06	6.81	6.71
3M′	89—90.8	69.00	69.06	6.73	6.71
3AB′	108—110	53.89	53.65	5.06	4.98
3A	94—95.5	65.87	65.87	6.34	6.40
3C	98—99	61.54	61.62	5.50	5.46
3B′	54.0—55.0	54.91	54.69	5.04	4.84
4H	43—46[b)] (52)[b,c)]	67.45	67.52	6.03	6.00
4A	49—50[b)] (53)[b,d)]	65.03	65.04	6.10	6.06
6	Oil				

a) Ref. 11a. b) Decomp point. c) Refs. 12a—c and e. d) Ref. 12d.

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$$k_t = k_\Delta^{\mathrm{H}} 10^{\rho_\Delta(\sigma^\circ + r_\Delta \Delta\bar{\sigma}_R^+)} + k_u^{\mathrm{H}} 10^{\rho_u(\sigma^\circ + r_u \Delta\bar{\sigma}_R^+)}$$

The best-fit correlations of the acetolysis were $\rho_\Delta=-4.29$ and $r_\Delta=0.59$ for the aryl-assisted process and $\rho_u=-1.38$ and $r_u=0.19$ for the aryl-unassisted process, as shown in Fig. 1.[10]

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