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Solvent Effects on the Solvolysis of Benzyl *p*-Toluenesulfonates[1)]

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Solvolysis rates of benzyl *p*-toluenesulfonate were determined in a wide variety of solvents. The solvent effects were analyzed based on the Winstein–Grunwald equation. The solvent effect on benzyl solvolysis failed to give a single linear correlation with the 2-adamantyl Y_{OTs} parameter. The lower response to the solvent polarity and the pattern of dispersion for each binary solvent series can be qualitatively interpreted in terms of nucleophilic solvent assistance. The Winstein–Grunwald analysis gave $m=0.67$ and $l=0.36$, but with less satisfactory precision. The use of the polarity scale Y_{neo} derived from 2-methyl-2-phenylpropyl solvolysis in place of Y_{OTs} gave an improved correlation. A solvent polarity scale Y_{neo} is better applicable to benzyl solvolysis than 2-adamantyl-based Y_{OTs}, since the former is compatible with the entire π-delocalization of cationic charge between aryl ring and the reaction center in the transition state.

The mechanism of the solvolytic displacement of substituted benzyl substrates is highly controversial, particularly with regard to the role of the solvent in the process. There are various approaches to investigate the mechanistic details of the benzyl solvolysis.[2—15)] We have investigated the precise mechanism based on the correlation analysis of the substituent effect.[6)] The Yukawa–Tsuno treatment provides a single smooth curved correlation; it thus strongly supports a k_c–k_s(or S_N1–S_N2) mechanistic transition with change in the ring substituent.[6)] The reduced ρ value can be utilized as a measure of solvent nucleophilic assistance. The solvolysis of benzyl tosylates (*p*-toluenesulfonates) exhibits a gradual change in mechanism from S_N1 for the range of strongly electron-donating substituents, through the borderline region, to the conventional S_N2 mechanism as the substituent becomes increasingly electron-withdrawing.[2—6)]

Another approach to investigate the mechanism is to apply solvent effect correlation analysis.[8—15)] The Winstein–Grunwald equation[8,16)] has generally been used as a mechanistic probe, especially for analyzing the extent of the involvement of solvent nucleophilicity in the solvolytic processes:[14)]

$$\log(k/k_{80\mathrm{E}}) = mY + lN, \qquad (1)$$

where k and $k_{80\mathrm{E}}$ are the rate constants in a given solvent and in the reference solvent (80 vol% aqueous EtOH), and Y and N are the solvent ionizing power and nucleophilicity parameters, respectively, m and l being the sensitivities to these parameters. The conventional Y_{OTs} and N_{OTs} parameter scales for the description of tosylate reactivities were defined, based on 2-adamantyl and methyl tosylates as reference substrates:[14,17)]

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

There is no doubt about the significant change with aryl substituents in the extent of nucleophilic involvement of solvent in the transition state for benzyl solvolysis in nucleophilic solvents. The mechanistic changeover between S_N1 and S_N2 mechanisms will usually take place somewhere within the range of variation of the aryl substituent, depending also on the nature of solvents. The k_c process expected for activated substrates can be readily differentiated by a large response (m value in Eq. 1 or 2) of the rate to the solvent polarity from the k_s process of deactivated substrates, with lower responses generally implying significant nucleophilic assistance. The solvolysis of a series of substituted benzyl tosylates will therefore be suitable as a model system for examining the validity of the Bentley–Schleyer characterization of solvolytic mechanisms and for confirming the concept of a continuous spectrum of k_s–k_c mechanisms.[14)]

The solvent effect on the solvolysis of benzyl tosylates was studied earlier by Winstein and co-workers,[8)] and most recently by Kevill in the ordinary solvolyzing solvents.[13)] Harris and others attempted to rationalize the complicated solvent dependence of the benzyl solvolysis in terms of mechanistic changes with the ring substituent.[12)] However, their simple pattern recognition analysis has provided only intuitive and qualitative interpretation for the mechanistic changeover. Furthermore, the data so far available in the literature[8—13)] are not sufficient for us to examine critically the applicability of the Schleyer-Bentley treatment (Eq. 2). Accordingly, we have carried out extensive studies concerning the dependence of the solvent effect upon aryl substituents in the solvolysis of substituted benzyl tosylates. In the present paper we will be concerned mostly with the behavior of the parent benzyl tosylate. We have also determined the solvolysis rates of *m*-methylbenzyl and *m*-chlorobenzyl tosylates in an extended range of solvents, and have analyzed the solvent effect in terms of Eq. 2.

Results

Solvolysis rates of unsubstituted benzyl, *m*-methylbenzyl, and *m*-chlorobenzyl tosylates were determined in a wide variety of solvents. The range of solvents covers aqueous binary solvent mixtures of ethanol, methanol, acetone, acetonitrile, dioxane, 2,2,2-trifluoroethanol (TFE), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and also includes ethanol–TFE mixtures (ET), acetic acid, and formic acid.

The rate measurement in aqueous organic solvents was usually carried out by conductimetric method and the determination in organic acid was made by the ordinary titrimetric method. The conductivity method is generally convenient for accurately determining the rate constants in the range of 10^{-5}—10^{-2} s^{-1} in most aqueous organic solvents; our precision was generally within 1.5 % reproducibility. The results are listed in Tables 1, 2, and 3, together with relevant literature data.

In Fig. 1, the solvolysis rates of benzyl tosylate at 25 °C are plotted, on a lograrithmic scale, against the 2-adamantyl-based Y_{OTs}. The solvent parameters used are listed in Table 4. No simple linear mY relationship was observed for the solvolysis of benzyl tosylate. Aqueous ethanol–aqueous methanol plots and aqueous acetone plots fall on separate lines of different slopes ($m_{\mathrm{EW}}=0.55$ for aq ethanol series and $m_{\mathrm{AW}}=0.77$ for aq acetone series) with a significant gap (0.65 log-unit at $Y_{\mathrm{OTs}}=0$), and the plots for less nucleophilic solvents, acids and fluorinated alcohols, lie below the aq alcoholic and acetone lines. The significantly lower m value than unity anticipated for the k_{c} substrate as well as the characteristic deviation pattern of non-nucleophilic solvents in the decelerating direction is at least qualitatively consistent with the interpretation in terms of the mechanistic involvement of the solvent nucleophilicity. However, the results of the correlation analysis with Eq. 2 as summarized in Table 5 cannot characterize the above dispersion behavior in terms of the response to the nucleophilicity of solvents. For the set of all solvents, a direct application of Y_{OTs} parameter fails to result in any satisfactory correlation, whereas the dual parameter Eq. 2 involving the nucleophilicity term results in a fairly improved correlation of $m=0.67$ with an l value of 0.36 (Entry 1 in Table 5). The susceptibility of benzyl tosylate to solvent nucleophilicity is quite comparable to that observed for isopropyl tosylate.[13c,14,18] However, the precision of the fit to Eq. 2 is not sufficiently improved to attain a practical criterion of the precision level of acceptable conformity. Particular dispersion for respective binary solvent series still remains clearly visible in the ($mY_{\mathrm{OTs}}+lN_{\mathrm{OTs}}$) plot for the unsubstituted benzyl tosylate (in Fig. 2). Entry 2, excluding the aqueous acetone series, can give no improved correlation with Eq. 2, whereas the set (Entry 3) consisting of aq acetone and less nucleophilic solvents gives an excellent correlation with a l value of 0.3. The set (Entry 4) consisting only of aq acetone and aq ethanol series results in a correlation with a high l value of ca. 1.8. This extraordinarily high l value[19] has already been criticized as a correlational artifact arising from the large discrepancy between the two main series of the above binary solvent mixture.[13b,20—22]

The solvent effects on solvolyses of m-methylbenzyl and m-chlorobenzyl tosylates also were analyzed in the same manner based on Eq. 2. Quite analogous results were obtained with a comparable precision to that for the unsubstituted one, as summarized in Table 5. The precision of the fit to Eq. 2 is again not sufficiently improved to attain a practical criterion of acceptable conformity. In contrast, the m-methyl derivative can be related linearly with the unsubstituted one with the aid of the solvent nucleophilicity term, $\log(k/k_{80\mathrm{E}})_{m\text{-Me}}=1.073\log(k/k_{80\mathrm{E}})_{\mathrm{H}}-0.110N_{\mathrm{OTs}}+0.016$; SD$=\pm0.043$ and $R=0.9991$. It is also apparent that m-chlorobenzyl results in an interrelation of excellent linearity with significant involvement of nucleophilicity to unsubstituted benzyl tosylate, with an excellent precision of $R=0.995$ and SD$=\pm0.079$; $\log(k/k_{80\mathrm{E}})_{m\text{-Cl}}=0.766\log(k/k_{80\mathrm{E}})_{\mathrm{H}}+0.342N_{\mathrm{OTs}}-0.025$.

The precise linearity among these three benzyl tosylates implies that there may be a common solvent polarity Y_{Bz} scale, as well as a common nucleophilicity scale N_{OTs}, capable of precisely describing the solvent effect characteristic of the benzyl solvolysis system.

The precision of the Winstein–Grunwald plots can be improved considerably by taking into account specific solvation effects, e.g., significant differences in solvation between aryl and alkyl substrates.[16a,16c,20—28] In order to account for the deviation from the mY correlation in terms of the nucleophilicity (lN) term, a reference Y_{Bz} scale particularly suitable to describing the polarity dependence (mY) term in this system is required:

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

We have demonstrated that the solvent polarity scale based on the neophyl (2-methyl-2-phenylpropyl) solvolysis is applicable not only to aryl-assisted solvolyses but also to the solvolyses of benzylic tosylates.[21,22] It has also been proposed that α-(t-butyl)benzyl tosylate is a suitable model compound for benzylic $\mathrm{S_N1}$ solvolytic reactivities.[25b,29] The extra solvation of aromatic rings can also be taken into account as a common factor in the comparison with such a benzylic reference solvolysis. The reference Y_{Bz} scales based on neophyl and p-methoxyneophyl tosylates[21] and α-(t-butyl)benzyl tosylate,[25b,29] in addition to the adamantyl-based Y_{OTs}, listed in Table 4 are utilized to analyze the present data based on Eq. 3; the correlation results are summarized in Table 6. The improvement of the precision of these Y_{Bz} correlations with Eq. 3 is significant compared with that of the correlation based on the conventional 2-adamantyl Y_{OTs}. The solvent effects in these benzyl solvolyses correlate best with the kinetic solvent polarity scale Y_{Bz} defined by the solvolysis of neophyl tosylate. In the correlation 3 using the neophyl Y_{Bz} scale (Y_{neo}) in Fig. 3, the plots for all binary sol-

Table 1. Rate Data of Solvolysis of Benzyl Tosylate[a]

Solv.[b]	$10^5\ k/\mathrm{s}^{-1}$ (Temp/°C)	$10^5 k/\mathrm{s}^{-1}$	$\Delta H^{\neq}_{25\,°\mathrm{C}}$[c]	$\Delta S^{\neq}_{25\,°\mathrm{C}}$[c]
		25 °C	kcal mol^{-1}	e.u.
30E	121.4(0), 528.9(15)	1378	15.1	−16.4
40E	33.18(0)	459.3	16.4	−14.2
50E	9.760(0), 484.5(35)	179.0, 200[d]	18.1	−10.4
60E	5.118(0), 628.7(45)	93.41, 97.4[d]	17.9	−12.5
70E		51.28, 55.4[d]		
80E	210.2(45)	29.59, 30.7,[d] 32.4[e]	17.9	−14.7
90E	110.2(45)	15.94	17.6	−16.8
EtOH	41.56(45)	5.357, 5.33[e]	18.7	−15.3
50M		599.0		
60M		296.7		
80M		79.35		
MeOH		17.84, 16.7[e]		
i-PrOH		2.153		
20A		1676		
30A	35.64(0)	485.9	16.3	−14.4
40A	9.139(0)	137.3	17.0	−14.8
50A	2.483(0), 294.4(45)	42.27	17.7	−14.5
60A	100.7(45)	13.33	18.5	−14.3
70A	35.49(45)	4.564	18.7	−15.5
80A	11.80(45)	1.410	19.4	−15.6
50D		51.81		
60D		16.82		
80D		1.69		
50AN		36.44		
60AN		15.26		
80AN		2.608		
90AN		0.5525		
30T		528.2		
40T		288.3		
50T		201.8		
70Tw		127.2		
80T	437.1(45)	74.44	16.1	−18.9
97Tw	3.035(0), 327.9(45)	47.51	17.4	−15.5
TFE		42.25		
20ET		19.52		
40ET		13.23		
60ET		10.26		
80ET		8.030		
97HFIPw		669.1		
50HFIP		220.8		
AcOH[f]		0.2694, 0.261,[g] 0.276[h]		
	5.51(50),[i] 62.9(75)[i]	0.315[i,j]		
HCOOH[f]	139(15),[k] 235(20),[k] 733(30)[k]	490,[i] 423[j,k]	18.8[k]	−6.5[k]

a) Conductimetrically determined, otherwise noted. b) Volume percent of first-named organic component, otherwise noted. Abbreviation, E=ethanol, A=acetone, M=methanol, AN=acetonitrile, D=dioxane, T=TFE=2,2,2-trifluoroethanol, HFIP=1,1,1,3,3,3-haxafluoro-2-propanol, and ET=Ethanol-TFE mixture (e.g., 20ET=20 vol EtOH : 80 vol TFE mixture). Suffix w means weight percent. c) 1 cal=4.184 J. d) Ref. 9. e) Ref. 8 at 25.05 °C. f) Titrimetrically determined. g) Ref. 8 at 25.05 °C in the presence of 0.20 wt% Ac_2O. h) Ref. 4. i) Ref. 3b. j) Extrapolated from rate data at other temperatures. k) Ref. 13c.

vent series are obviously coalesced into a single straight-line correlation. This contrasts sharply with the significantly dispersed Y_{OTs}–N_{OTs} plot in Fig. 2. A single linear correlation with Y_{Bz}–N_{OTs} makes the deviations of EtOH, 90E (90 vol% aqueous EtOH), MeOH, and 2-propanol points even more significant, but the reason for the deviations of these solvents is unknown at present. If these solvents of high alcohol content are excluded, the precision of the fit of Eq. 3 is improved to $R \geqq 0.98$ and SD$\leqq$0.17 (Table 6).

Discussion

The present benzyl solvolysis shows a considerably lower response (m value) to the solvent polarity of any

Table 2. Rate Data of Solvolysis of *m*-Methylbenzyl Tosylate[a)]

Solv.[b)]	10^5 k/s^{-1} (Temp/°C)	10^5k/s^{-1}	$\Delta H^{\neq}_{25°C}$ [c)]	$\Delta S^{\neq}_{25°C}$ [c)]
		25 °C	kcal mol^{-1}	e.u.
30E	341.4(0), 1422(15)	3230	14.0	−18.4
40E	72.76(0)	1004	16.4	−12.7
50E	20.10(0)	350.2	17.9	−9.7
60E	9.489(0)	169.5	18.1	−10.6
70E	5.161(0), 623.5(45)	91.12	17.8	−12.7
80E	2.729(0), 340.8(45)	50.09	18.0	−13.5
90E	1.354(0), 173.1(45)	25.26	18.0	−14.5
EtOH	66.46(45)	8.989	18.3	−15.8
50M	101.6(0)	1347	16.1	−13.0
60M	43.02(0)	627.0	16.8	−12.4
80M	9.112(0)	151.4	17.6	−12.4
MeOH	1.574(0)	30.33	18.6	−12.4
i-PrOH		3.148		
30A	85.60(0)	1137	16.2	−13.3
40A	19.58(0)	279.4	16.6	−14.5
50A	4.723(0), 540.0(45)	78.69	17.6	−13.7
60A	174.4(45)	22.93	18.5	−13.0
70A	60.91(45)	7.460	19.2	−13.0
80A	18.12(45)	2.262	19.0	−16.0
50D		96.80		
60D		28.69		
80D		2.55		
50AN		74.37		
60AN		30.14		
80AN		4.717		
90AN		0.9378		
30T	153.7(5)	1527[d)]		
40T		856.8		
50T	63.15(5)	627.2	18.3	−7.2
70Tw		420.7		
80T	17.75(0)	265.0	16.9	−13.6
97Tw	10.96(0)	194.7	18.0	−10.5
TFE		168.0		
20ET		56.66		
40ET		28.75		
60ET		19.53		
80ET		13.38		
97HFIPw		3498		
50HFIP		892.5		
AcOH[e)]	4.47(40)[f)]	0.5767, 0.872[g)]		
HCOOH[e)]		1430[h)]		

a)b)c) See footnotes a,b, and c in Table 1. d) Estimated value from the rate constant at 5 °C based on linear log k relation between 5 and 25 °C for aq TFE series. e) Titrimetrically determined. f) Ref. 4. g) Ref. 3b, estimated value based on the rate constant at 40 °C in Ref. 4. h) Ref. 3b.

binary solvent series than that of close to unity for the limiting k_c solvolysis. There is remarkable dispersion of the plot against the conventional Y_{OTs} for binary aqueous solvent series, accompanied by downward deviations for weak nucleophilic solvents. It is likely that there is no simple linearity against the 2-adamantyl-based Y_{OTs}, in the so-called borderline solvolyses where nucleophilic assistance is apparently important. The dispersion for binary solvent mixture series in Fig. 1 may be plausibly interpreted in terms of relatively higher nucleophilicities of alcoholic mixtures than those of non-alcoholic ones, whereas the less significant deviations of solvents of distinctly low nucleophilicity are in fact inconsistent with the significant separation between alcoholic and non-alcoholic lines. The points for aqueous TFE and EtOH–TFE mixtures in Fig. 1 are within 0.5 in log k unit from the main correlation lines. Obviously, the plot in Fig. 2 displays little improvement of the fit to Eq. 2 when the lN term for the solvent nucleophilicity is included. The Bentley–Schleyer treatment based on Y_{OTs} and N_{OTs} parameters has only limited applicability to the solvolyses of benzyl tosylates. There seems to be a distinct difference between benzylic substrates and simple aliphatic substrates, e.g., 2-adamantyl tosylate, in

Table 3. Rate Data of Solvolysis of m-Chlorobenzyl Tosylate$^{a)}$

Solv.$^{b)}$	$10^5\ k/s^{-1}$ (Temp/°C)	$10^5 k/s^{-1}$ 25 °C	$\Delta H^{\neq}_{25°C}$ $^{c)}$ kcal mol^{-1}	$\Delta S^{\neq}_{25°C}$ $^{c)}$ e.u.
30E		63.77		
40E		26.91		
50E	94.04(45)	13.22	17.9	−16.3
60E	56.75(45)	8.563	17.2	−19.4
70E	41.47(45)	5.583	18.3	−16.6
80E	28.81(45)	3.833	18.4	−17.0
90E	6.733(35), 42.53(55)	2.342	18.2	−18.8
EtOH	7.897(45)	0.9370, 0.9853$^{d)}$	19.5	−16.2
50M		41.08		
60M		24.70		
80M		9.102		
MeOH		2.663		
i-PrOH	3.152(45), 35.48(75)	0.4788$^{f)}$	17.2	−25.3
20A		68.85		
30A		23.67		
40A		8.386		
50A		3.217		
60A		1.30$^{d)}$		
70A		0.578$^{d)}$		
80A	0.686(35),$^{d)}$ 1.975(45), 4.76(55)$^{d)}$	0.2557$^{e)}$	18.5	−22.0
50D		3.702		
60D		1.476		
80D		0.256		
50AN		2.406		
60AN		1.212		
80AN		0.3004		
90AN	0.6170(45), 7.115(75)	0.09197$^{f)}$	17.3	−28.0
30T		14.87		
40T		7.879		
50T		5.243		
70Tw		2.926		
80T	3.985(35), 10.52(45)	1.414$^{f)}$	18.3	−19.3
97Tw	5.411(45), 8.442(55)	0.5081	18.3	−21.2
TFE		0.4706		
50HFIP		2.790		
97HFIPw		1.732		
80ET		1.210		
60ET		1.266		
40ET		1.088		
20ET		0.7757		
AcOH$^{d)}$	3.51(75),$^{g)}$ 29.6(99.8)$^{g)}$	0.0162,$^{g,f)}$ 0.0136$^{h)}$	21.6$^{g)}$	−17.2$^{g)}$
HCOOH$^{d)}$		5.33$^{g)}$		

a)b)c) See footnotes a,b, and c in Table 1. d) Titrimetrically determined. e) Ampoule technique with conductivity determination (see Experimental). f) Extrapolated from other temperatures. g) Ref. 3b. h) Ref. 4.

the solvent-effect behavior of the limiting k_c mechanism. Similar dispersion behavior for different binary solvent series has been pointed out for the solvent effects on solvolyses of benzylic precursors,[16a,16c,20—28] leading to a pessimistic conclusion about the definition of a generally applicable kinetic solvent scale for S_N1 reactions.[23] Indeed, the neophyl solvolysis as well as relevant aryl-assisted solvolyses which are mechanistically independent of any nucleophilic solvent assistance show nonlinear response to the solvent polarity Y_{OTs}.[20,21] Nonlinear $\log k$ vs. Y_{OTs} plots were also found for solvolyses of α-arylvinyl derivatives.[22] Bentley et al. particularly note that their treatment with Eq. 2 should be applied exclusively to simple saturated alkyl substrates, which do not yield resonance-stabilized carbocations and do not undergo neighboring group participation.[14]

The Winstein–Grunwald correlation (Eq. 1) of the solvolysis of benzyl tosylate can be appreciably improved as seen in Fig. 3, when either neophyl tosylate[20,21] or α-(t-butyl)benzyl tosylate[29] is used as a reference Y_{Bz} substrate instead of 2-adamantyl tosylate; as clearly shown in the Y_{neo} plot of Fig. 4, the separation between aqueous acetone and aqueous ethanol lines is significantly reduced, and the extent to

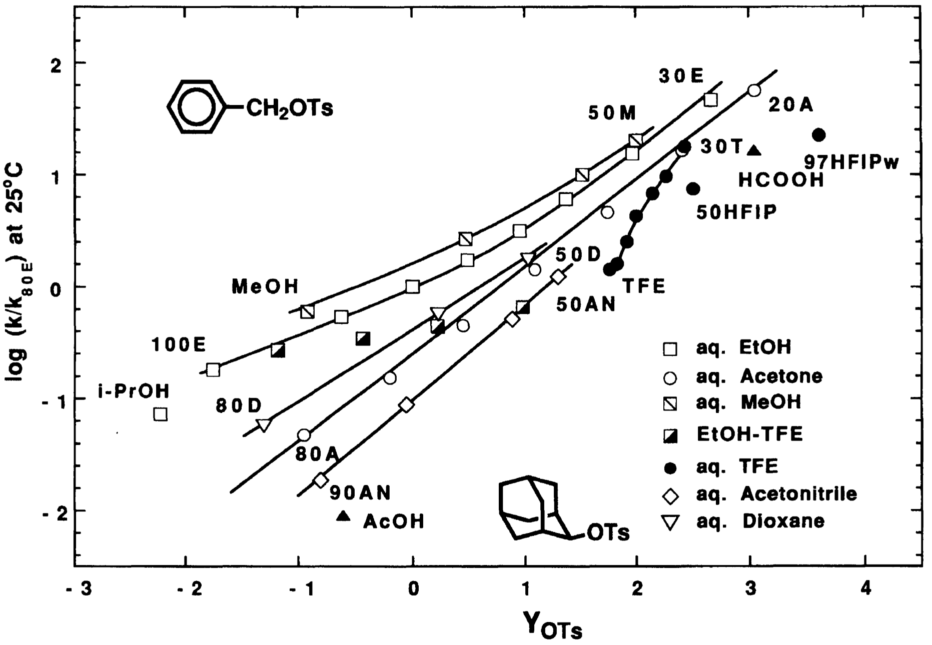

Fig. 1. The mY_{OTs} plots for solvolysis of benzyl tosylate.

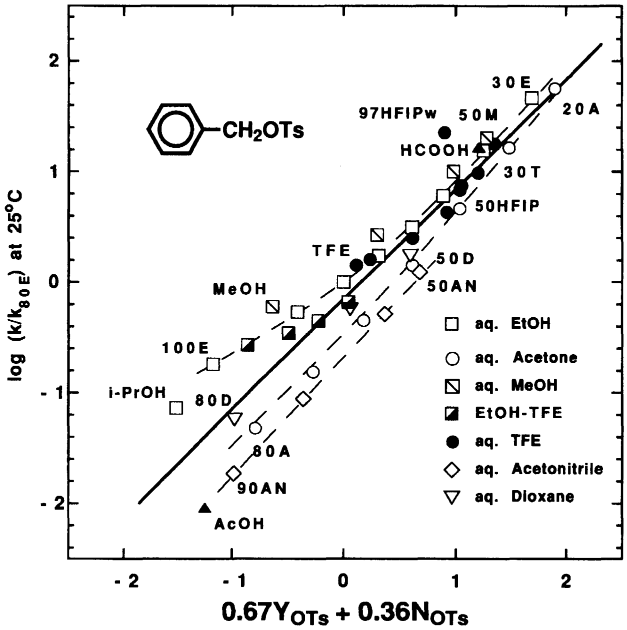

Fig. 2. The $(mY_{\text{OTs}}+lN_{\text{OTs}})$ plots for solvolysis of benzyl tosylate.

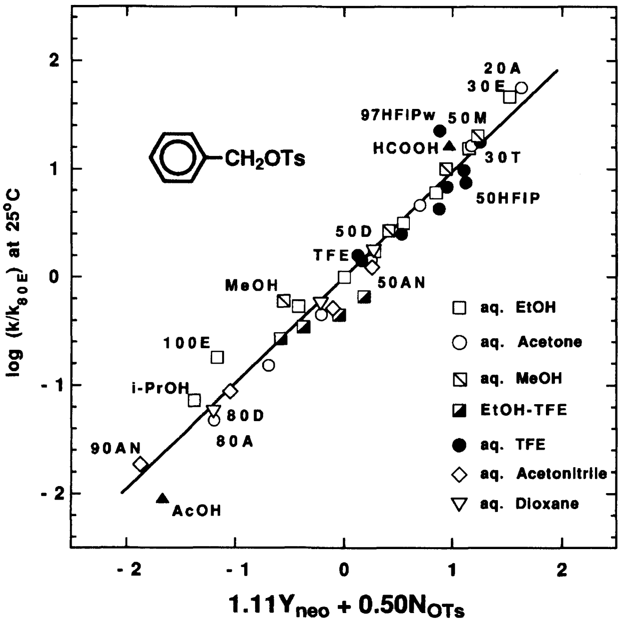

Fig. 3. The $(mY_{\text{neo}}+lN_{\text{OTs}})$ plots for solvolysis of benzyl tosylate.

which the plots for non-nucleophilic or very weakly nucleophilic solvents deviate downward from the ethanol and acetone lines can now be accounted for even quantitatively by the N_{OTs} parameters of solvents. The dispersion of the Y_{OTs} plots for various series of aqueous binary solvent mixtures observed in Fig. 1 should be due not simply to the solvent nucleophilicity (the lN term) but also to certain other factors associated with the benzylic S_N1 ionization process (involved in the mY term). The 2-adamantyl-based Y_{OTs} parameter is completely free of mechanistic involvement of solvent nucleophilicity in the rate-determining transition state, whereas Y_{OTs} shows limited applicability to the correlation analysis of benzylic k_c solvolysis systems.

A wide range of "dispersion" phenomena have been rationalized by differences in solvation between aromatic and aliphatic derivatives.[16a,16c,20—28] The conventional Y_{OTs} parameter based on the solvolysis of 2-adamantyl tosylate reflects the solvent effect on the solvolyses to form a localized, highly congested carbocation which demands an extensive external stabilization

Table 4. Solvent Parameters[a)]

Solv.[b)]	Y_{OTs} 25 °C	N_{OTs}	Y_{neo}[c)] 45 °C	Y_{Δ}[d)] 45 °C	$Y_{t\text{-Bu}}$[e)] 25 °C
EtOH	−1.75	0.00	−1.055	−0.790	−1.280
90E	−0.62	0.01	−0.395	−0.281	−0.489
80E	0.00	0.00	0.000	0.000	0.000
70E	0.49	−0.05	0.274	0.223	0.433
60E	0.95	−0.09	0.537	0.394	0.815
50E	1.37	−0.11	0.816	0.612	1.247
40E	1.97	−0.22	1.137	0.833	1.816
30E	2.67	−0.31	1.513	1.117	2.526
MeOH	−0.92	−0.04	−0.487	−0.368	−0.326
80M	0.47	−0.05	0.394	0.298	0.719
60M	1.52	−0.13	0.904	0.735	1.581
50M	2.00	−0.19	1.196	0.928	2.011
i-PrOH	(−2.23)	−0.06	(−1.22)	−1.008	−2.028
80A	−0.95	−0.42	−0.889	−0.823	−0.946
70A	−0.20	−0.38	−0.456	−0.454	−0.317
60A	0.45	−0.34	−0.039	−0.120	0.298
50A	1.09	−0.35	0.381	0.199	0.915
40A	1.75	−0.39	0.813	0.546	1.552
30A	2.43	−0.40	1.240	0.909	2.240
20A	3.05	−0.44	1.669	1.237	(2.84)
80D	−1.30	−0.29	−0.954	−0.833	−1.338
60D	0.25	−0.26	−0.083	−0.111	0.079
50D	1.03	−0.29	0.373	0.311	0.778
50AN	1.31	−0.57	0.488	0.320	1.089
60AN	0.89	−0.64	0.192	0.091	0.697
80AN	−0.01	−0.90	−0.539	−0.408	−0.103
90AN	(−0.80)	−1.24	(−1.1)	−0.828	−0.811
TFE	1.76	−3.0	1.504	1.277	2.059
97Tw	1.83	−2.79	1.374	1.123	2.031
80T	1.92	−1.90	1.342	1.092	2.058
70Tw	2.00	−1.20	1.336	1.068	(2.08)
50T	2.15	−1.14	1.373	1.081	2.129
40T	2.27	−0.92	1.410	1.111	2.219
30T	2.43	−0.80	1.494	1.152	2.405
80ET	(−1.18)	−0.19	−0.443	−0.393	−0.722
60ET	−0.44	−0.55	−0.092	0.015	−0.100
40ET	0.21	−1.01	0.413	0.454	0.603
20ET	0.98	−1.72	0.943	0.824	1.329
97HFIPw	3.61	−4.27	2.730	2.088	4.247
50HFIP	2.51	−1.78	1.816	1.424	2.704
AcOH	−0.61	−2.35	−0.443	−0.325	−0.731
HCOOH	3.04	−2.35	1.940	1.706	2.855

a) Data taken from Refs. 14, 20, and 21, otherwise determined here. The values in parenthesis are estimated from the appropriate linearity. b) See footnote b in Table 1. c) $Y_{\mathrm{neo}}=\log(k/k_{\mathrm{80E}})_{\mathrm{Neophyl\ OTs}}$. d) $Y_{\Delta}=\log(k/k_{\mathrm{80E}})_{p\text{-}\mathrm{Methoxyneophyl\ OTs}}$. e) $Y_{t\text{-Bu}}=\log(k/k_{\mathrm{80E}})_{\alpha\text{-}(t\text{-}\mathrm{Butyl})\mathrm{benzyl\ OTs}}$.

from the solvent. The transition state for a benzylic cation formation is stabilized by π-delocalization of cationic charge into the aryl group, and hence it requires less stabilization by external solvation. It is highly likely that the effective charge dispersal causes a significant loss of the highly oriented specific solvation at the reaction center and a significant change in the relative importance of cation/anion solvations. This must be the important cause of dispersion of the mY plot. In practice, we need an appropriate reference Y_{Bz} scale based on the delocalized carbocation solvolysis, in order to achieve a quantitative estimation of the $\mathrm{S_N1}$ and $\mathrm{S_N2}$ character of the transition state of the solvolysis of benzyl tosylates. The present study clearly shows that the polarity scale Y_{Bz} based on the *p*-methoxyneophyl or neophyl solvolysis, which of course involves a highly delocalized cationic transition state, can be applied to the solvolyses of benzyl tosylates. The neighboring aryl group in the anchimeric assistance mechanism plays the role of an intramolecular nucleophile displacing the leaving group, from the rear side of the reaction center, and the transition state of the aryl-assisted solvolysis is structurally quite close to the trigonal-bipyramidal transition state of the $\mathrm{S_N2}$ displacement reaction with a fixed incoming nucleophile. The neophyl solvolysis of the Y_{Bz} scale based thereon models most reasonably the solvent polarity effect on the entirely charge-delocalized transition state of a spectrum of carbocationic $\mathrm{S_N2}$ solvolyses of benzyl tosylates.

The extent of the nucleophilic solvent assistance can be evaluated more accurately as the deviation from the expected behavior only when the proper Y_{Bz} parameter is used. This enables us to examine the actual validity of N_{OTs} parameters. Kevill introduced a set of nucleophilicity parameters, N_{KL}, based on the triethyloxonium ion solvolysis and demonstrated its applicability to the solvent effect correlations of various solvolyses.[13)] In particular, for the solvolysis of substituted benzyl tosylates, better correlations with Eq. 2 were reported by using the N_{KL} parameter instead of using the conventional N_{OTs} parameter.[13d)] Applying this type of modification for N value, we can achieve much better results for these benzyl tosylates, to lend some support for Kevill's previous conclusion,[30)] whereas the better results do not immediately lead to a conclusion about the inadequacy of N_{OTs} parameter values. We often see that the $\mathrm{S_N2}$ solvolyses exhibit nonlinear responses to the conventional nucleophilicity N_{OTs} scale based on the methyl tosylate solvolysis.[18)] The importance of the involvement of solvent nucleophilicity may vary as a quadratic function of the solvent nucleophilicity, implying the enhanced shift in mechanism with solvents.[18)] There is considerable doubt about whether or not the linearity of the solvent nucleophilicity holds over a wide range of substituted benzyl series. Further examination will be necessary of the solvolysis of strongly deactivated benzyl tosylates, where the solvent nucleophilicity plays a more important role.

The present results of Winstein–Grunwald analysis lead to a conclusion that the solvolysis of benzyl tosylates having moderately enhanced reactivity shows intermediate responses to both the solvent polarity and the solvent nucleophilicity. Conformity to Eq. 3 or the additivity of the polarity mY and the nucleophilicity lN terms points to a single-step displacement mechanism for any benzyl tosylates, and it appears difficult

Table 5. Results of Correlation Analysis by Eq. 2[a)]

No.	Solvents	m	l	c	$R^{b)}$	SD[c)]	$n^{d)}$
Unsubstituted benzyl tosylate							
1.	All solvents	0.67±0.04	0.36±0.06	−0.16	0.939	±0.33	42
2.	Exc. AW[e)]	0.67±0.04	0.38±0.06	−0.09	0.935	±0.33	35
3.	Exc. EW-MW-ET[f)]	0.80±0.03	0.27±0.04	−0.59	0.987	±0.17	25
4.	AW and EW[g)]	0.73±0.04	1.78±0.31	0.11	0.984	±0.18	15
m-Methylbenzyl tosylate							
5.	All solvents	0.72±0.05	0.27±0.06	−0.16	0.937	±0.35	41
6.	Exc. AW[e)]	0.72±0.05	0.30±0.07	−0.08	0.939	±0.35	35
7.	Exc. EW-MW-ET[f)]	0.87±0.03	0.19±0.04	−0.61	0.986	±0.19	24
8.	AW and EW[g)]	0.75±0.05	1.85±0.34	0.13	0.981	±0.19	14
m-Chlorobenzyl tosylate							
9.	All solvents	0.51±0.03	0.61±0.05	−0.15	0.933	±0.28	42
10.	Exc. AW[e)]	0.50±0.04	0.63±0.05	−0.09	0.930	±0.28	35
11.	Exc. EW-MW-ET[f)]	0.60±0.02	0.52±0.03	−0.53	0.985	±0.14	25
12.	AW and EW[g)]	0.58±0.03	1.80±0.27	0.07	0.979	±0.16	15

a) $\log(k/k_{80E}) = mY_{OTs} + lN_{OTs} + c$. b) Correlation coefficients. c) Standard deviations. d) Numbers of data points involved. e) Excluding aqueous acetone series. f) Excluding *i*-PrOH, aqueous ethanol, aqueous methanol, and ethanol–TFE mixtures. g) Partial correlation for aqueous ethanol and aqueous acetone series.

Table 6. Correlation Analysis by Eq. 2 or 3

Y_{Bz}[a)]	Solvents	m	l	c	$R^{b)}$	SD[c)]	$n^{d)}$
m-Methylbenzyl tosylate							
Y_{OTs}	All	0.72±0.05	0.27±0.06	−0.16	0.937	±0.35	41
	Exc. E, 90E, M[e)]	0.82±0.04	0.27±0.05	−0.33	0.959	±0.29	37
$Y_{t\text{-Bu}}$	All	0.80±0.03	0.39±0.05	−0.17	0.972	±0.24	41
	Exc. E, 90E, M[e)]	0.87±0.03	0.39±0.03	−0.28	0.984	±0.18	37
Y_{neo}	All	1.19±0.04	0.43±0.04	0.00	0.983	±0.19	41
	Exc. E, 90E, M[e)]	1.25±0.03	0.42±0.03	−0.08	0.990	±0.14	37
$Y_{\triangle}$	All	1.50±0.05	0.46±0.04	0.04	0.979	±0.21	41
	Exc. E, 90E, M[e)]	1.57±0.05	0.46±0.04	−0.02	0.984	±0.18	37
Unsubstituted benzyl tosylate							
Y_{OTs}	All	0.67±0.04	0.36±0.06	−0.16	0.939	±0.33	42
	Exc. E, 90E, M[e)]	0.76±0.04	0.35±0.05	−0.32	0.960	±0.27	38
$Y_{t\text{-Bu}}$	All	0.75±0.03	0.46±0.04	−0.17	0.972	±0.23	42
	Exc. E, 90E, M[e)]	0.80±0.03	0.46±0.03	−0.28	0.983	±0.18	38
Y_{neo}	All	1.11±0.04	0.50±0.04	−0.01	0.980	±0.19	42
	Exc. E, 90E, M[e)]	1.16±0.03	0.50±0.03	−0.08	0.987	±0.15	38
$Y_{\triangle}$	All	1.41±0.05	0.54±0.04	0.03	0.976	±0.21	42
	Exc. E, 90E, M[e)]	1.47±0.05	0.54±0.04	−0.02	0.980	±0.19	38
m-Chlorobenzyl tosylate							
Y_{OTs}	All	0.51±0.03	0.61±0.05	−0.15	0.933	±0.28	42
	Exc. E, 90E, M[e)]	0.58±0.03	0.61±0.04	−0.27	0.954	±0.24	38
$Y_{t\text{-Bu}}$	All	0.57±0.03	0.69±0.04	−0.16	0.966	±0.20	42
	Exc. E, 90E, M[e)]	0.61±0.03	0.69±0.03	−0.24	0.976	±0.18	38
Y_{neo}	All	0.84±0.04	0.72±0.04	−0.03	0.970	±0.19	42
	Exc. E, 90E, M[e)]	0.89±0.04	0.72±0.03	−0.09	0.977	±0.17	38
$Y_{\triangle}$	All	1.07±0.05	0.75±0.04	0.00	0.969	±0.19	42
	Exc. E, 90E, M[e)]	1.12±0.05	0.75±0.04	−0.04	0.973	±0.19	38

a) $\log(k/k_{80E}) = mY_{Bz} + lN_{OTs} + c$. $Y_{t\text{-Bu}} = \log(k/k_{80E})_{\alpha\text{-}(t\text{-Butyl})\text{benzyl OTs}}$, $Y_{neo} = \log(k/k_{80E})_{\text{Neophyl OTs}}$, and $Y_{\triangle} = \log(k/k_{80E})_{p\text{-methoxyneophyl OTs}}$. b) Correlation coefficients. c) Standard deviations. d) Numbers of data points involved. e) Excluding the data in *i*-PrOH, EtOH, 90E, and MeOH.

to fit the solvent-effect behavior of these benzyl substrates into the classical S_N1–S_N2 framework. The wide variation of the l/m ratio with substituents suggests a variation in the extent of nucleophilic solvent assistance

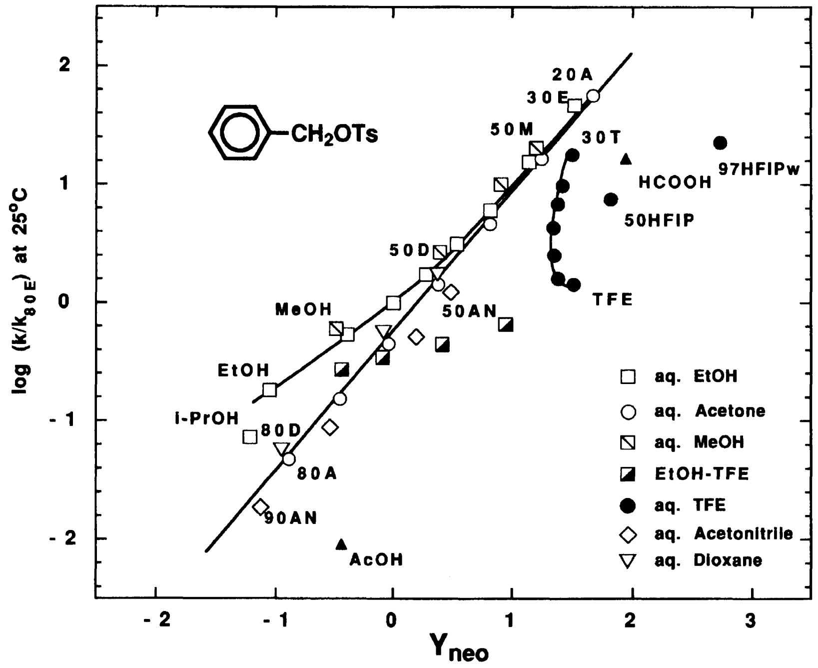

Fig. 4. The mY_{neo} plots for solvolysis of benzyl tosylate.

in the S_N2 transition state, namely a new mechanistic scheme of a continuous spectrum of "intermediate S_N1–S_N2 mechanism," with a clear mechanistic distinction between S_N1 and S_N2 reactions. The mechanistic spectrum can reasonably interpret the relatively high m and appreciable l values observed for the benzyl borderline solvolysis. Schleyer and Bentley assumed that simple secondary substrates for which there was evidence for nucleophilic assistance by solvent nucleophile and evidence for a reaction intermediate forming solvated ion pairs in the rate-determining step undergo solvolysis by a "S_N2 (intermediate)" mechanism.[31] This new mechanism may be considered to have a dissociative bimolecular displacement structure in the rate-determining transition state, and the transition state lies close to the carbocationic end in a continuous spectrum of S_N2 mechanisms of varying tightness.

According to the classical framework of solvolysis mechanisms, on the other hand, simultaneous occurrence of S_N1 and S_N2 mechanisms should result in a clear deviation from the exact linear correlation (for Eqs. 1, 2, and 3), since the solvolysis rate constant for such a system should be given by a sum of the rate constants for competing S_N1 and S_N2 processes. Richard and Jencks have argued for the simultaneous occurrence of classical S_N1 and S_N2 processes, based on the independent evidence from the product selectivity analysis.[10] Kevill also prefers the superimposition of S_N1 and S_N2 mechanisms rather than intermediate mechanism,[13a] but no evidence appears definitive. Nevertheless the pattern of dispersion of the mY plot is not in line with the simultaneous occurrence of simple classical S_N2 and S_N1 mechanisms, at least for these substituted derivatives of borderline region. This can be readily demonstrated by a simulation analysis setting the overall rates as a sum of competing rates of a typical S_N1, e.g., 2-adamantyl tosylate, and a classical S_N2 process, e.g., methyl tosylate. The significant downward deviations of the plot for aqueous TFE can not be related to the competition scheme of classical mechanisms. Presumably, the incomplete conformity to the dual parameter treatment (Eq. 2 or 3), e.g., accompanied by the deviations of EtOH, 90E, MeOH, and *i*-PrOH might be accounted for by the competition scheme of this S_N2 (intermediate) and classical S_N1 mechanisms, while the deviation from the correlation 3 with proper Y_{Bz} is too small to warrant interpretation.

The role of ion-pair intermediates in solvolyses has received much attention. They can cause deviations from expected solvent effect behavior. The term "S_N2 (intermediate)" emphasized the possibility that an S_N2 reaction may proceed via a nucleophilically solvated ion-pair intermediate without any internal return.[14,31] This mechanism may be energetically more feasible than the Sneen ion-pair S_N2 mechanism,[32] while the absence of internal return in solvolysis of simple secondary substrates has already been criticized.[33] In the recent ^{18}O scrambling study, internal return has been shown to be operative to different extents in most of the solvolyses of typical benzylic tosylates[7b,34] and many simple secondary alkyl tosylates as well as for 2-adamantyl tosylate.[33,35] Most important, significant internal return was observed in the solvolysis of unsubstituted benzyl tosylate in acetic acid, aqueous TFE, and to a slightly lesser extent in aqueous acetone and aqueous ethanol.[7b] This argues strongly against the operation of any single (intermediate) mechanism proceeding through an essentially non-dissociative rate-determining transition state, in the moderately solvent-assisted solvolysis of benzyl tosylates. If the S_N2 (intermediate) mechanism occurs without internal return as assumed by Bentley et. al.,[31] the present benzyl solvolysis should have occurred through the S_N2 (intermediate) mechanism competing with the classical S_N1 machanism, accompanied by significant internal return. The Sneen unified ion-pair mechanism also is clearly not supported, since the ion-pair return obviously diminishes as the S_N1 character is decreased with electron-attracting substitutent.[7b] The investigation should be extended to the solvent effects on the wider range of substituted members of this series.

Experimental

Materials: Benzyl tosylates were prepared by the Schotten–Bauman method,[4] as described before[6a] and were recrystallized from ether–hexane; unsubstituted derivative, mp 57.4—58.0 °C, lit,[3b] mp 58—59 °C, 58.5—58.9 °C.[36] Anal. Found: C, 63.97; H, 5.17%. Calcd for $C_{14}H_{14}O_3S$: C, 64.10; H, 5.38%. *m*-Methyl derivative, recrystallized from ether–petroleum ether, mp 60.2—61.0 °C, lit,[3b] mp 60.5—61.5 °C, 65.1—65.5 °C.[36] Anal. Found: C, 65.30; H, 5.86%. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.84%. *m*-Chloro derivative, recrystallized from ether–hexane, mp 81.3—82.0 °C, lit,[3b] mp 80.5—81.5 °C, 81—83 °C,[4] 81.5—82 °C.[2b] Anal. Found: C, 56.63; H, 4.46%. Calcd for $C_{14}H_{13}O_3SCl$: C, 56.66; H, 4.42%.

Anhydrous acetic acid, acetone, dioxane, ethanol, methanol, 2,2,2-trifluoroethanol, and water were purified as described before.[20,21,24,37] 2-Propanol was refluxed with aluminum isopropoxide and fractionated. Acetonitrile (spectral grade) was refluxed with P_2O_5, distilled onto Na_2CO_3, and fractionated through Widmer column. 1,1,1,3,3,3-Hexafluoro-2-propanol (purity>99.99%) offered from Central Glass Co., Ltd., was directly employed without further purification.

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

Kinetic Measurement: Solvolyses in aqueous binary solvents were followed conductimetrically.[20,21,24] Conductance measurements were made using approximately 25 or 50 cm^3 of 10^{-3}—10^{-4} $mol\,dm^{-3}$ solution of the starting tosylate in a thermostatted bath at an appropriate temperature controlled within ±0.01 °C. For a conductivity measurement in aqueous solvent of high water content, complete dissolution can be attained relatively quickly by first dissolving the substrate in a small amount of the organic solvent to the respective aqueous organic solvents added an adjustable amount of water. Conductance readings were taken automatically by using a conductivity meter (CM-50AT and CM-60S, Toa Electronics Ltd.). Solvolyses were followed by taking at least 100 readings at appropriate intervals for 3 half-lives, and the infinity reading was taken after 10 half-lives. The precision of fit to first-order kinetics was generally satisfactory over 3 half-lives ($R>0.99998$). The rates of solvolysis for less reactive substrate were followed by using the ampoule technique with conductivity determination. The ester solution of a similar concentration was made up and sealed in twenty (5 ml) ampoules for one run. The ampoules were allowed to react in a thermostatted bath and the reaction was stopped by withdrawing an ampoule and immersing it in ice water at appropriate intervals for 2.5 half-lives. Several ampoules were allowed to react for 10 half-lives to provide an infinity conductivity reading. The ampoules were fitted with a conductivity cell; after equilibration at 25 °C, the conductivity readings were taken using a conductivity meter.

The rates of acetolysis and several slow solvolysis rates were determined by the ordinary titrimetric method using the usual ampoule technique.[37]

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

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