Substituent Effects. XX.[1)] Highly Electron-Deficient Carbocation Solvolyses[2)]

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(Received October 11, 1989)

The solvolysis rates of 1-aryl-2,2,2-trifluoroethyl tosylates (**1**-OTs) and *m*-nitrobenzenesulfonates (**1**-ONs) were determined conductometrically in aqueous ethanol and aqueous TFE. While the Brown $\rho^+\sigma^+$ equation does not give a simple linear plots, but a remarkably split pattern, there is a linear free energy relationship between the solvolyses of **1**-OTs and 1-aryl-1-(trifluoromethyl)ethyl tosylates (**2**) with a slope of unity over a wide range (10^8 in reactivity) of substituents from *p*-MeO to unsubstituted derivatives. The substituent effect on the solvolysis of **1** should be closer to that on the solvolysis of **2**, rather than to the σ^+ substituent effect. The ρ value for this system was estimated to be identical to the value of -6.3 assigned for **2**, and the r value in the LArSR correlation to be comparable with or even higher than the r=1.4 of **2**. The enhanced r value of this system must be caused from a strong destabilization of the transition state by the α-CF_3 substituent. Extremely high ρ^+ values have recently been pointed out for many solvolyses generating highly electron-deficient carbocations; however, in no case is the ρ^+ value equally high for the electron-attracting region of the substituent. In fact, they all resulted in significantly concave σ^+ plots, suggesting a mechanistic transition. All of the conflicts must be attributed to the inadequacy of the simple application of σ^+. The use of the Brown σ^+ scale must be the only cause of a curve break in the correlation plot of such a system having a significantly different resonance demand.

In the foregoing paper,[1)] we analyzed the substituent effect on the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates (**2**) in terms of our LArSR Eq. 1[3)]

$$\log k/k_0 = \rho(\sigma^0 + r\Delta\bar{\sigma}^+_R) \qquad (1)$$

The substituent effect on this extremely electron deficient benzylic system can be reasonably described in terms of Eq. 1 with a high resonance demand r=1.39.[1,4)] Significant deviation from a linear σ^+ correlation indicates that this highly electron-deficient system is far beyond the scope of the simple Brown $\rho^+\sigma^+$ treatment. The Brown σ^+ scale should be referred to as a good average of the resonance demands for solvolyses generating ordinary stable benzylic carbocations. Nevertheless, Liu et al. particularly emphasized that the accelerating derivatives in this solvolysis gave a good σ^+ correlation with an extremely high ρ^+ value of -10, in contrast with -6.3 for the deactivating substituent range.[5)] Our recent studies on the gas-phase stabilities of benzylic carbocations indicate that the stabilities of 1-aryl-1-(trifluoromethyl)ethyl cations do not give a linear relation against those of the corresponding α-cumyl (1-methyl-1-phenylethyl) cations.[4,6)] The α-CF_3 carbocation should have an intrinsically higher resonance demand than the α-cumyl cation.[4a,c,6)] Such an enhanced resonance demand would generally be anticipated for relevant extremely electron-deficient carbocation systems.

Recently, Tidwell et al. reported that the substituent effect on the solvolysis of strongly deactivated 1-aryl-2,2,2-trifluoroethyl tosylates (**1**-OTs) gave ρ^+ values of -9—-12 in most solvents, but a value of -6.7 in trifluoroacetic acid (TFA), based on a simple $\rho^+\sigma^+$ treatment.[7)] The large negative ρ^+ value was taken as evidence for the k_c mechanism, and was attributed to a strong destabilization of the incipient cation by the α-CF_3 group.[7)] However, a distinctly smaller ρ^+ value in TFA than in other solvents can hardly be interpreted in any ordinary mechanistic terms. In order to achieve an appropriate analysis of the substituent effect on this system, an enhanced resonance demand due to a strong deactivation by α-CF_3 should be taken into account in terms of the LArSR Eq. 1. The literature data appear to be insufficient to draw any decisive conclusion concerning either the substituent effect behavior or the mechanistic characteristics of this solvolysis. Accordingly, we have determined the solvolysis data for a more extended series of substituents of this secondary electron-deficient carbocationic system and analyzed the substituent effect on this system.

Results

The solvolysis rates of 1-aryl-2,2,2-trifluoroethyl tosylates (**1**-OTs) and *m*-nitrobenzenesulfonates (**1**-ONs) were determined conductometrically in aqueous ethanol and aqueous trifluoroethanol. The solvolysis rates of strongly deactivated substrates were measured by using the *m*-nitrobenzenesulfonates (nosylates) instead of using tosylates, and were calibrated to the rates of tosylate solvolysis according to the linear relationships; for the solvolysis in 50 vol% aqueous ethanol (50E),

$$\log k_{OTs} = (1.027 \pm 0.004) \log k_{ONs} - 1.509, \qquad (2)$$

and for the solvolysis in 97%(w/w) trifluoroethanol

(97%TFE),

$$\log k_{\mathrm{OTs}} = (1.029 \pm 0.038) \log k_{\mathrm{ONs}} - 1.220. \qquad (3)$$

The results are summarized in Tables 1 and 2. The σ^+ plot for the solvolysis of **1** in 50E in Fig. 1 displays no simple linear relationship but, rather, shows a remarkably split pattern. The gap of 1.5 log units between two lines is too large to be referred simply to as experimental error. Tidwell et al. estimated a ρ^+ value of −10, based only on the two data points of *p*-MeO and *p*-methyl substituents for solvolysis in aqueous ethanol, assuming a linear σ^+ correlation.[7] A simple inspection of Fig. 1, however, indicates that the ρ^+ value depends upon the choice of substituents, and Tidwell's assumption of a linear σ^+ correlation is not in line with the present figure. The σ^+ plots of strong π-donor substituents construct a partial linear correlation with a ρ value of ca. −6, which is much lower than the value determined by the *p*-MeO—*p*-Me line, but nearly identical to that given for the TFA set. A major conflict appears to arise from the insufficient data base as well as a result of the inadequacy of a simple application of the σ^+ scale. On the other hand, LArSR Eq. 1 provides a reasonable interpretation for the split σ^+ plot. A series of strong *p*-π-donors which have comparable $\Delta\bar{\sigma}_R^+$ values (=−0.7) should give an exact ρ^+ value as a slope of the plots against ordinary σ^+ values, since the $r\Delta\bar{\sigma}_R^+$ term remains constant for these substituents, irrespective of r value of the system. The same is true for a series of para alkyl substituents, all having constantly small $\Delta\bar{\sigma}_R^+$ values (−0.1—−0.2). The significant gap between the two lines for both classes of substituents evidently points to a higher r value for this system.

The substituent effect on this system can be compared with the substituent effect of a structurally

Table 1. Solvolysis of 1-Aryl-2,2,2-trifluoroethyl Tosylates in 50% (w/w) Aq Ethanol

Substituent	Temp/°C	$10^5 k_t$/s^{-1}		$\Delta H^{\ddagger}_{25\,°C}$ [a]	$\Delta S^{\ddagger}_{25\,°C}$ [a]
		1-OTs	**1**-ONs[b]	kcal mol^{-1}	e.u.
4-MeO-3-Me	0.00	199.8			
	15.00	1305			
	25.00	4106[c]		19.0	−1.2
p-MeO	0.00	47.39			
	25.00	934.3		19.2	−3.4
p-MeS	0.00	6.760			
	25.00	146.1		19.3	−6.8
p-PhO	25.00	14.53		21.2	−4.9
	45.00	147.2			
4-MeO-3-Cl	0.00		14.85		
	25.00	10.97	415.5	22.4	−3.3
	45.00	113.4		(21.0)	(0.9)
2-Fluorenyl.	25.00	13.82			
4-MeS-3-Cl	0.00		3.873		
	25.00	2.887	110.8	21.4	−7.4
	45.00	29.87		(21.3)	(−0.7)
3,4,5-Me$_3$	25.00	0.4241[c]		22.5	−7.8
	45.00	4.893			
	65.00	42.27			
4-MeO-3-CN	25.00	0.1441[c]		23.0	−8.2
	45.00	1.760			
	65.00	15.98			
3,4-Me$_2$	25.00	0.110[c]		23.5	−6.9
	45.00	1.424			
	65.00	13.59			
4-MeS-3-CN	25.00	0.06537[d]	2.801		
p-Me	25.00	0.03660[c]	1.597	23.8	−8.0
	45.00	0.4888	22.09	(24.2)	(0.7)
	75.00	13.65			
p-Et	25.00	0.02455[d]	1.080	(23.7)	(−1.8)
	45.00		14.20		
p-*t*-Bu	25.00	0.00801[d]	0.3889[c]	(24.0)	(−2.8)
	45.00		5.285		
	65.00		52.75		
3,5-Me$_2$	25.00	0.000640[d]	0.0309[c]	(25.0)	(−4.6)
	45.00		0.465		
	75.00		14.19		

a) 1 cal=4.184 J. Activation parameters in parentheses are for **1**-ONs at 25 °C. b) *m*-Nitrobenzenesulfonates. c) Extrapolated from rate constants at other temperatures. d) Calculated from linear logarithmic rate relation between tosylates and nosylates at 25 °C by Eq. 2.

Table 2. Solvolysis of 1-Aryl-2,2,2-trifluoroethyl Tosylates in 97% (w/w) Aq Trifluoroethnol

Substituent	Temp/°C	10^5k_t/s^{-1}		$\Delta H^{\ddagger}_{25\,^\circ\mathrm{C}}$ [a]	$\Delta S^{\ddagger}_{25\,^\circ\mathrm{C}}$ [a]
		1-OTs	**1**-ONs[b]	k cal mol^{-1}	e.u.
p-MeO	25.00	5970[a]			
p-MeS	0.00	67.60			
	25.00	937.4		16.5	−12.5
p-PhO	25.00	262.5			
2-Fluorenyl.	25.00	207.9			
4-MeO-3-Cl	25.00	60.68	1268		
4-MeS-3-Cl	25.00	22.41	381.0		
3,4,5-Me$_3$	25.00	2.850			
4-MeO-3-CN	25.00	0.08319[b]		20.3	−18.2
	45.00	0.7653			
	75.00	13.24			
3,4-Me$_2$	25.00	0.607[b]		19.5	−17.0
	45.00	5.120			
	65.00	33.54			
p-Me	25.00	0.110[a]	2.543	(21.1)[d]	(−8.9)[d]
	45.00		25.33		
p-*t*-Bu	25.00	0.06607[c]	1.513		
3,5-Me$_2$	25.00	0.003342[c]	0.05609[b]	(23.1)[d]	(−9.5)[d]
	45.00		0.6954		
	75.00		17.65		
H	25.00	0.0000804[c,e]	0.00222[b]	(23.7)[d]	(−14.0)[d]
	65.00		0.285		
	100.00		8.47		

a) Ref. 7. b) Extrapolated from rate constants at other temperatures. c) Calculated from the linear logarithmic rate relation between tosylates and nosylates at 25 °C (Eq. 3). d) Activation parameters for *m*-nitrobenzenesulfonates. e) Ref. 7, 1.48×10^{-9}s^{-1}.

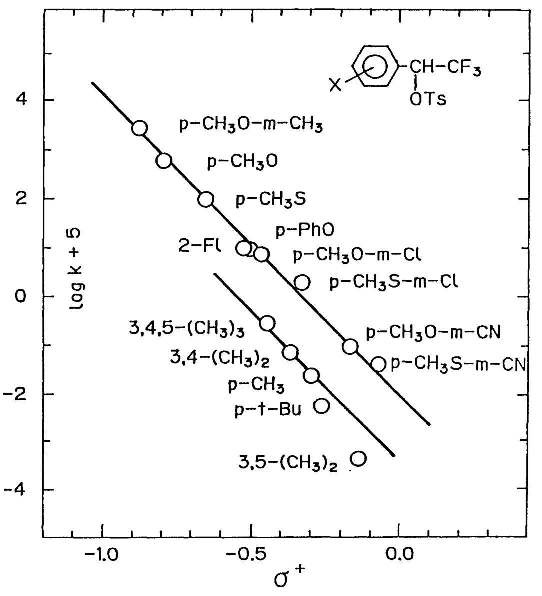


Fig. 1. σ^+ plot for solvolysis of 1-aryl-2,2,2-trifluoroethyl tosylates (**1**-OTs) in 50% aq EtOH at 25 °C.

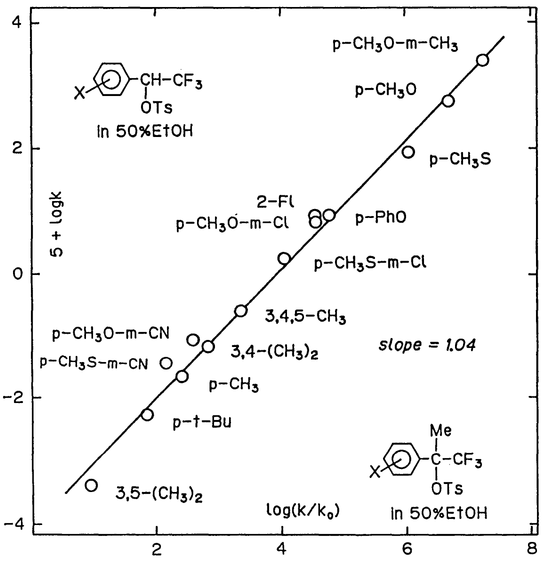


Fig. 2. Linear free energy relationship between **1** and **2** in 50% EtOH.

similar, destabilized-carbocation solvolysis of **2**. There is in fact a linear logarithmic rate relationship between solvolyses **1** and **2** in 50% aq EtOH with a slope of unity covering a range of 10^7 reactivity from 4-MeO-3-Me to 3,5-dimethyl derivatives, as shown in Fig. 2. A linear correlation is also observed for the solvolysis of **1** in 97% aq TFE against the solvolysis rates of **2** in 80%(v/v) aq TFE,[8] over a reactivity range of 10^7—10^8 down to the unsubstituted derivative, as shown in Fig. 3. This linear plot is in sharp contrast with the scattered σ^+ plot in Fig. 1. The substituent effect in the present system **1** is closer to that on the solvolysis of **2**, rather than to the so-called σ^+-substituent effect on the α-cumyl solvolysis. The ρ value for this system should be identical to the value of −6.3 for **2**, and the r value should also be approxi-

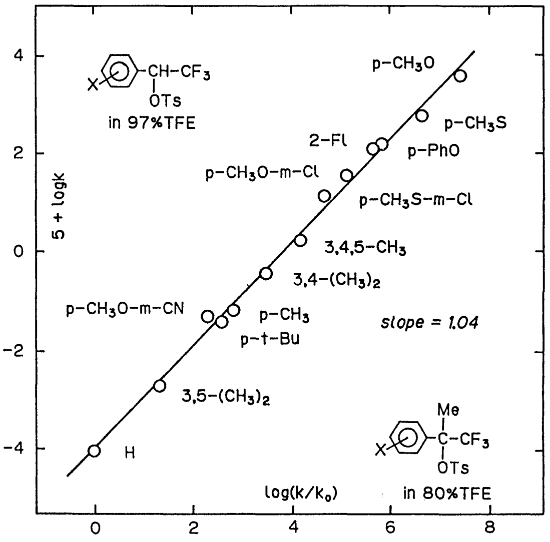


Fig. 3. Linear free energy relationship between **1** and **2** in aq TFE.

mately the same as that for **2**; if the downward separation of alkyl groups in Fig. 2 is regarded as being significant, the r value may be even higher for **1** than that of 1.39 for **2**, though a minor difference in the r value is not important in the present discussion. The same conclusion can likewise be drawn from the plot in a highly polar TFE solvent in Fig. 3. Both ρ and r values are considered to be essentially constant regardless of solvents. This conclusion conflicts with the previously reported one.7) It is worth noting that the LArSR ρ value is essentially identical with the exceptional, low ρ^+ value observed for the TFA set,7) for which no reasonable explanation has been given based on the simple Brown σ^+ analysis.

Discussion

From a comparison of the plots in Figs. 1 and 2, the substituent effect on this system **1** is much closer to that on the solvolysis of a similarly deactivated tertiary system **2**, rather than to the Brown σ^+ substituent effect. A slope of unity of the plot argues against the high ρ^+ value of -10 estimated for **1** in most solvents, but even argues for the ρ^+ value of -6 of the exceptional TFA case.7) It should be noted that in the aq. alcoholic sets, the substituent range on which the ρ^+ values were based differs from the range applied in TFA. This may lead to an alternative interpretation that the ρ^+ value for the activated region of substituents (p-MeO to p-Me) is remarkably higher than that for the deactivated region from H to m-CF$_3$. Such a nonlinear behavior is just what would be expected for a mechanistic shift with a substituent change, as observed in the benzyl solvolysis.9)

It is likely that an S$_N$1-S$_N$2 mechanistic transition occurs in this electron-deficient secondary system, whereas the ρ_A^+ value of -6.3 for the acceptor region of substituent should be too large to refer to the S$_N$2 mechanism. The σ^+ plot in Fig. 1 for the solvolysis in 50E is even inconsistent with the previous conclusions given in the literature.7) Most important, there is no reason to conclude from this discontinuous σ^+ relationship that a single mechanism operates in this system for the whole range of substituents. These inconsistencies must arise merely from the intrinsic deficiency of the simple σ^+ treatment. The enhanced r value in this system should be caused primarily from an enhanced destabilization of the incipient carbocation or the transition state by the electronegative α-CF$_3$ substituent.

The LArSR Eq. 1 may be applied directly to this solvolysis of **1** in 50E, to provide a good correlation with $\rho=-6.05$ and $r=1.53$.10) Since the range of substituent points is not wide enough, the accuracy of this correlation can not be discussed in detail. However, the results are all quite consistent with the above conclusion. As described for the correlation analysis of the solvolysis of **2**,1,4a,d) the significance of the r value can be examined most reasonably by the dependence of the goodness of the fit upon varying the r value. The SD vs. r curve for this system in 50E is shown in Fig. 4 in comparison with that for **2** in 80E. The steepness of the wedge plot for **1** indicates a high reliability of the LArSR correlation of the solvolysis of **1**, and is nearly identical with that observed for the solvolysis of **2**, suggesting a comparable reliability of ca. ±0.05 for the r value of the LArSR correlation. The r value of 1.5 assigned for this system is therefore reliable to be statistically distinguished from the value of unity for the σ^+ system. The LArSR correlation analysis provides a clear indication of a high reson-

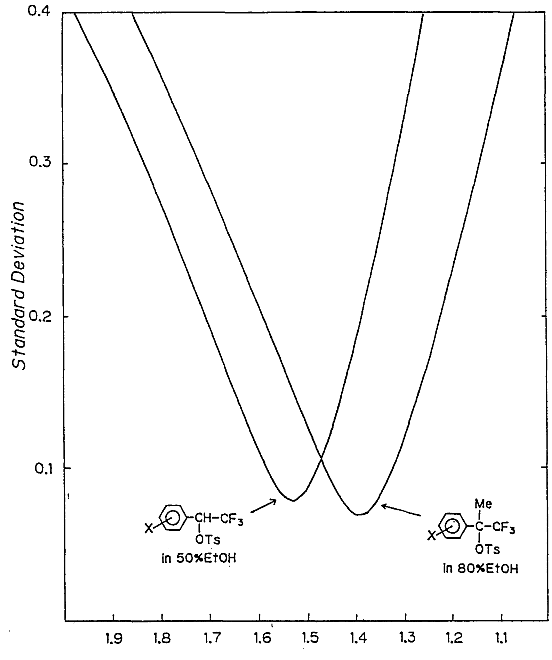


Fig. 4. Plots of SD as a function of r for the solvolysis of **1**-OTs in 50E and **2** in 80E.

ance demand (r=1.5) for this system, but it does not support Liu's conclusion that a simple Brown σ^+ correlation gives a similar result.5)

The correlation analysis of the substituent effect for the TFE set is hardly achieved by a direct application of Eq. 1, because of a significant solvent modification of the substituent parameters in TFE. However, we can define the correlation using a modified LArSR treatment (4),

$$\log k/k_0 = \rho[\bar{\sigma}_s + (r - \bar{r}_s)\Delta\bar{\sigma}_R^+], \qquad (4)$$

where $\bar{\sigma}_s$ corresponds to a set of apparent substituent constants and $\bar{r}_s$ to the r value of a reference system. Furthermore, the $\rho\bar{\sigma}_s$ term can be practically replaced by the $\log k/k_0$ values of the reference system. Using the solvolysis of **2** in 80% aq. TFE8) as a reference system, we can obtain a good linear relationship,

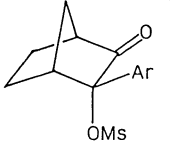
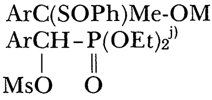
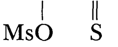
$$\log (k/k_0)_{1,97T} = 0.96 \log (k/k_0)_{2,80T} - 0.77\Delta\bar{\sigma}_R^+,$$

with a precision of R=0.999 and SD=±0.11. From the ρ value of −7.056 and r of 1.41 for the reference system **2**,8) the ρ value is estimated to be −6.8 and the r value to be 1.5 as the difference in resonance demand ($r-\bar{r}_s$)=0.1: The r value may be slightly more exalted in **1** rather than **2**, while the ρ value must be identical in both systems. This is in sharp contrast with the previous conclusion of the ρ^+ value of −10 in the literature.7)

The ρ^+ value of −10 is, in fact, comparable with the ρ value estimated by the LArSR analysis of the intrinsic cation stability in the gas phase.4,6,11) The solvolytic transition state in the solution phase must be stabilized by solvation and should give rise to a lower response to the substituent change than the intrinsic response of unsolvated carbocations in the gas phase. It is difficult to account for the lack of attenuation of the substituent response despite their inevitable, strong solvation of the strongly destabilized transition states.

Substituent effects on other relevant, strongly deactivated carbocationic systems can be similarly interpreted based on the LArSR Eq. 1; the ρ^+ values for relevant solvolyses in the literature are summarized in Table 3. The remarkably high ρ^+ value was emphasized to be a characteristic feature of highly electron-deficient carbocation reactions and, in fact, extremely high (negative) ρ^+ values of <−10 are observed for five systems out of the ten relevant destabilized systems in Table 3. Thus, Tidwell concludes that the range of −10 to −12 appears to be at least a temporary ceiling on the magnitude of ρ^+ values for benzylic solvolyses.12) However, it should be realized that all of these high ρ^+ values were determined only for the range of electron-donating substituents of negative σ^+. In no case can the effects of electron-attracting substituents be satisfactorily described by the high ρ_D^+ values

Table 3. Substituent Effects of Benzylic Solvolyses at 25 °C

System	Solv.	$\rho_D^{+a)}$	$\rho_A^{+a)}$	Slope$^{b)}$	R
ArC(CN)Me-OMs$^{c)}$	TFE	−6.70	−6.70	0.881	0.998
ArC(CF$_3$)$_2$-OTs$^{d)}$	TFA	−10.7		1.12	0.999
ArC(CN)CF$_3$-OTs$^{d)}$	TFA	−12.1		1.32	
e) 	EtOH	−5.69	−4.15	0.726	0.998
ArC(CF$_3$)Me-OTs$^{f)}$	80E	−8.8	−6.4	1.000$^{g)}$	
ArC(CF$_3$)Me-Br$^{h)}$		−10.3			
ArC(SO$_2$Ph)Me-OMs$^{i)}$	MeOH	−8.0		0.921	0.9999
ArC(SOPh)Me-OMs$^{i)}$	TFE	−7.2		0.778	0.9995
 $\mathrm{ArCH(OMs){-}P(=O)(OEt)_2}^{j)}$	TFE	−10.1	−6.1	0.918	0.993
	97HFIP	−10.3		1.123	0.9998
 $\mathrm{ArCH(OMs){-}P(=S)(OEt)_2}^{k)}$	AcOH	−7.15	−2.99	0.69$^{l)}$	0.985
				0.45$^{m)}$	0.9988
ArCH(CF$_3$)OTs$^{n)}$	TFA	−6.7	−6.7	1.05	0.993
	97HFIP	−9.1		1.020	0.994
	TFE	−9.8		1.046	0.997
	AcOH	−10.1		1.08	
	aq EtOH	−11.9—−9.7		0.982	0.998

a) ρ_D^+ and ρ_A^+ are ρ^+ values for electron-donor and -acceptor substituents, respectively. b) A slope of logarithmic rate relation against the $\log k$ for the solvolysis of ArCMe(CF$_3$)OTs in 80E1) whereas data in the fluorinated solvents were correlated with those for the solvolysis of **2** in 80%(v/v) aq TFE.8) c) Ref. 13. d) Refs. 12 and 16. e) Ref. 17. f) Refs. 1, 2, and 5. g) By definition. h) Ref. 5b. i) Ref. 18. j) Ref. 14. k) Ref. 15. l) Reactive than 3,4-Me$_2$. m) Less reactive than 3,4-Me$_2$. n) Ref. 7 and present work.

based on the electron donating groups. Whereas an extremely high ρ^{+}_{D} value of −10 was reported for the reactive region of the substituent for **2**, a ρ^{+}_{A} value of −6.4 (i.e., of more ordinary size) was given for the region of electron-attracting substituents.[5] In the present system **1**, the exceptionally small $\rho^{+}=-6.7$ given for the TFA set is the ρ^{+}_{A} value based only on electron-attracting substituents. Likewise, the ρ^{+} value of −6.70 for α-cyano-α-arylethyl mesylates in TFE[13] based on meta and π-accepting para substituents is not exceptional. Clearly, the ρ^{+}_{A} values defined for the attracting substituents are of ordinary size for all the data sets available. Thus, the apparent ceiling for the magnitude of the ρ^{+}_{A} value for electron-attracting substituents should not exceed −7 for any benzylic solvolyses. This conclusion is in serious disagreement with the literature generalization of a higher ceiling value of −10—−12. More seriously, the simple σ^{+} analysis leads to a generalization that strongly deactivated benzylic solvolyses without exception involve a mechanistic change with a break in the σ^{+} plot near the unsubstituted derivative. All of the conflicts appear to arise from an inadequate application of the σ^{+} scale.

While the substituents involved in these studies are in no case sufficient for a direct analysis by the LArSR Eq. 1, these substituent effects can be treated with the apparent $\bar{\sigma}$ value derived from the solvolysis of **2**, instead of with the Brown σ^{+}. More conveniently, the analysis has been carried out by using directly the $\log k/k_0$ for **2**, as listed in Table 3. Quite clearly, all of the 15 sets (except one in Table 3) give good linear relationships of a correlation coefficient >0.99, and none shows a significantly higher slope than unity. For the solvolysis of ArCH(OMs)PO_3Et_2,[14] a good linear free energy correlation is obtained against $\log k$ for the solvolysis of **2** in 80%TFE with a slope of 0.92 without significant break. There is no indication of a mechanistic change with substituents in this reaction. On the other hand, the solvolysis of ArCH(OMs)PS$(OEt)_2$[15] is the only case which shows a clear curve break in the plot against solvolysis of **2**, and evidently indicates a significant thio-group participation for deactivating substrates, as supported by other experimental results.[15] It should be emphasized that the use of the Brown σ^{+} scale is the only cause of a curve break in the substituent effect plot of systems having a significantly different resonance demand, in many cases pointing to a mechanistic transition.

These results suggest that the extremely high ρ^{+} values reported for these systems are simply an artifact of improper substituent effect analysis. The high ρ^{+} values were originally reported with special comment that because of the small number of points in these σ^{+} correlations the slopes should be interpreted with caution.[7] These original data do not appear to be sufficiently reliable as evidence to justify any large negative ρ^{+} value in relevant highly electron-deficient systems. The present examination evidently confirms that a different set of substituent constants with a high resonance demand should be required for linearly describing the substituent effects for these extremely electron-deficient benzylic systems. This is just the same approach as the Brown σ^{+}, instead of σ, which was introduced to properly describe the substituent effects on solvolysis producing relatively stable benzylic cations.

The present study provides definite answers to the controversy against the basic concept of varying resonance demands in the LArSR analysis. Liu et al. noted that most systems favored by the Yukawa–Tsuno LArSR treatment are secondary substrates in nucleophilic solvents and that such systems may also be subject to nucleophilic solvent participation.[5a] However, the preference of Eq. 1 for secondary systems is irrelevant to the mechanistic involvement of the solvent. We have recently shown that an identical r value is required for the solvolyses of α-methyl and α-*t*-butylbenzyl systems.[19] The r parameter generally shows little or no variation within a category of closely the same structure of the transition state, or of essentially the same mechanism.[3,20] It is quite reasonable that the solvolyses of α,α-dialkylbenzyl *p*-nitrobenzoates mostly provide excellent linear correlations against the Brown σ^{+}, indicating $r=1.0$ as being a good approximation.[21] Thus, the reason for our choice of secondary carbocation systems to study is simply because any significantly different r value can only be anticipated for systems other than those generating stable tertiary carbocations.

The LArSR correlations for a series of typical benzylic solvolyses are summarized in Table 4. The resonance demand significantly increases as the carbocation becomes destabilized. The ρ value tends to increase slightly with enhanced deactivation of incipient cation to attain a ceiling value of −7, which is in all the case distinctly lower than the reported ρ^{+} values based on σ^{+} analysis. The LArSR correlations for the gas-phase stabilities of the corresponding carbocations have become available from our recent studies by ion cyclotron resonance mass spectroscopy.[6,11] The ρ values for the gas-phase stabilities of benzylic cations are essentially constant, independent of parent carbocations.[4a,b,6,11] On the other hand, the r value varies significantly with parent systems and, most

Table 4. LArSR Correlations for Benzylic Solvolyses, $ArC^{+}(R^1)R^2$ at 25 °C

R^1,R^2	Me,Me[a)]	*t*-Bu,H[b)]	Me,H[c)]	H,H[d)]	Me,CF_3[e)]	H,CF_3[f)]
r	1.00	1.09	1.15	1.28	1.39	1.53
ρ	−4.59	−5.54	−5.45	−5.23	−6.29	−6.05

a) Ref. 22, in 90% aq acetone. b) Ref. 19, in 80% aq acetone (80A). c) Refs. 3b and c, in 80A; LArSR ρ value corrected to 25 °C. d) Ref. 23, in 80A. e) Ref. 1, in 80E. f) In 50E.

important, the r values for the gas phase carbocation stabilities are exactly the same as those observed in the solvolyses of the corresponding precursors.[4a,b,6,11) Varying resonance demand should be an essential feature of processes generating conjugative carbocations as well as a basic requirement for adequately describing the substituent effects.

The LArSR correlation analysis basically requires nonlinearity (or randomness) between σ^0 and $\Delta\bar{\sigma}_R^+$ parameters, and especially, for distinguishing between the LArSR and Brown σ^+ analyses, the nonlinearity between σ^+ and $\Delta\bar{\sigma}_R^+$ should be considered severely. As far as typical π-donor substituents of general use are concerned, there is an intrinsic close-linearity between the Brown σ^+ constants and any set of apparent substituent constants. Generally, most σ^+ correlations so far involve a few typical strong p-π-donors. Because of the crude linearity between σ^+ and $\Delta\bar{\sigma}_R^+$ inherent in these p-π-donors, the stronger ones located at the most reactive end in the σ^+ plot tend to deviate significantly only at that end responding to the r value of the system. Any system having an extremely high resonance demand, like the present system, should give a significantly high ρ^+ value for the σ^+ plot for the electron-donating region of substituents; when the attracting substituents are involved, they result in a concave σ^+ plot indistinguishable from the curvature associated with mechanistic shift. Thus, the deviation behavior of strong p-π-donor substituents of less negative σ^+ values disturbing the σ^+ versus $\Delta\bar{\sigma}_R^+$ linearity is most effective in distinguishing the cause of a nonlinear σ^+ plot and, in particular, to accurately estimate the r value. A combination of different classes of π-donors is essential for a precise LArSR analysis.[3c,4,20,24)

Finally, a significant break of the σ^+ plot is not necessarily related to the mechanistic change with a substituent change. Although the σ^+ may be a good average of the substituent constants applicable to the ordinary solvolysis generating stable carbocations, the resonance demand varies remarkably with the systems, and is quite often far beyond the scope of the simple Brown $\rho^+\sigma^+$ treatment. The σ^+ treatment may cause a significant curve break in the substituent effect correlation plot in most cases for any highly electron-deficient carbocation systems.

Experimental

Materials. 1-Aryl-2,2,2-trifluoroethanols: Substituted α,α,α-trifluoroacetophenones (29 mmol)[1) in 50 cm^3 of MeOH were reduced to corresponding alcohols with 2.2 g (26 mmol) of $NaBH_4$ and 6 cm^3 of 1 M NaOH (1 M=1 mol dm^{-3}) in 50 cm^3 of MeOH in an ice bath, according to literature procedure.[7) The crude alcohol was purified by silica-gel chromatography and directly used for the preparation of sulfonates.

4-MeO-3-CN and 4-MeS-3-CN derivatives were prepared by the conversion of bromo derivative by the Friedman–Shechter method.[25) The 4-MeO-3-Br or 4-MeS-3-Br alcohol was refluxed with copper(I) cyanide (2 eq.) in DMF for 6 h. The reaction mixture was decomposed with $FeCl_3$–HCl, extracted with benzene, and purified by column chromatography on silica gel.

1-Aryl-2,2,2-trifluoroethyl Arenesulfonates:[7) A solution of 1-aryl-2,2,2-trifluoroethanol (13.6 mmol) in 20 cm^3 of ether was slowly added to 1.6 g (33 mmol) of NaH in 20 cm^3 of ether under nitrogen atmosphere in an ice bath and the solution was stirred for 1 h. Then, 2.8 g (13.6 mmol) of toluenesulfonyl chloride in 30 cm^3 of ether was dropwise added to the flask and the mixture was stirred overnight. The ethereal solution was filtrated and concentrated under

Table 5. Physical Data of 1-Aryl-2,2,2-trifluoroethyl Arenesulfonates

Subst.	Mp/°C	Carbon/%		Hydrogen/%		Nitrogen/%	
		Found	Calcd	Found	Calcd	Found	Calcd
Tosylates (**1**-OTs)							
4-MeO-3-Me	68.0— 68.3	54.73	54.54	4.65	4.58		
p-MeO	55.5— 57.0[a)	53.33	53.33	4.24	4.20		
p-MeS	88.2— 89.2	51.03	51.06	3.96	4.02		
p-PhO	83.5— 85.0	59.96	59.71	4.09	4.06		
4-MeO-3-Cl	97.5— 98.5	48.74	48.68	3.60	3.57		
2-Fluorenyl	107(decomp)	63.82	63.15	4.24	4.10		
4-MeS-3-Cl	92.5— 93.0	46.79	46.77	3.47	3.43		
3,4,5-Me_3	99.5—100.5	58.36	58.14	5.32	5.14		
3,4-Me_2	103.0—103.5	58.04	58.06	5.11	5.14		
4-MeO-3-CN	130.0—131.5	53.00	52.99	3.66	3.66	3.68	3.63
p-Me	85.5— 85.8[b)	55.92	55.81	4.46	4.39		
m-Nitrobenzenesulfonates (**1**-ONs)							
4-MeO-3-Cl	81.0— 81.5	42.29	42.32	2.65	2.60	3.29	3.29
4-MeS-3-Cl	75.0— 78.0	40.92	40.78	2.51	2.51	3.07	3.17
p-Me	74.0— 76.2	47.93	48.00	3.27	3.22	3.73	3.73
p-t-Bu	68.0— 71.0	51.80	51.80	4.43	4.35	3.36	3.36
3,5-Me_2	98.0— 99.0	49.48	49.36	3.69	3.62	3.49	3.60
H	78.5— 79.5	46.55	46.54	2.80	2.79	3.83	3.88

a) Lit ,[7) mp 55—56 °C. b) Lit, [7) mp 81.5—82 °C.

vacuum. The precipitate was recrystallized from ether-hexane. The *m*-nitrobenzenesulfonates were prepared in the same way by using *m*-nitrobenzenesulfonyl chloride. Physical constants and analytical data are summarized in Table 5.

Solvents: Ethanol (95%) was dehydrated twice by heating under reflux with magnesium ethoxide and distilled. Commercial 2,2,2-trifluoroethanol was dried over Molecular Sieves 4A, heated under reflux with $CaSO_4$ and K_2CO_3, and fractionated through a Widmer column.[26] Deionized water was refluxed with $KMnO_4$ and the distillate was redistilled immediately before use.

50% aqueous ethanol (50E) was prepared by mixing equal volumes of ethanol and water at 25 °C. 97% (w/w) trifluoroethanol (97%TFE) was prepared by mixing corresponding weights of trifluoroethanol and water.

Kinetic Measurement. Solvolysis rates in aqueous organic solvents were measured by the ordinary conductometric method, as described before.[1,26] Conductivity readings were taken by using a conductivity meter (CM-50AT equipped with time interval unit and printer, TOA Electric Ltd.). The rates of solvolysis for less reactive substrates at higher temperatures were followed by using the ampoule technique with conductivity determination. The first-order rate constants were determined by the least-squares computer program; the precision of the fit to first-order kinetics was generally satisfactory, with correlation coefficient>0.99999 over 2.5 half-lives of the reaction.

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