April, 1990] © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 1129—1137 (1990) 1129

Substituent Effects. XIX.1) Solvolysis of 1-Aryl-1-(trifluoromethyl)ethyl Tosylates2)

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(Received October 11, 1989)

The rates of solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates were determined in 80% aqueous ethanol for a series of substituents. The Brown $\rho^+\sigma^+$ treatment fails to give a simple linear plot, but all the *p*-π-donors deviate upward from the meta-correlation line. On the other hand, the Yukawa-Tsuno LArSR Eq. gives a linear correlation over the whole range of substituents, $\log(k/k_0)=-6.287(\sigma^\circ+1.388\Delta\bar{\sigma}_R^+)$, with excellent precision. Strong destabilization of the carbocation intermediate by α-CF_3 appears to be reflected only in the extremely high *r* value, but not in the ρ value of the substituent effect. This conflicts seriously with the conclusion in the literature given for this reaction based on a simple Brown σ^+ treatment. This reaction, having an extremely high resonance demand $r=1.4$, should be far beyond the scope of the simple Brown σ^+ analysis. Varying resonance demand should be a basic requirement for adequately describing the substituent effect regarding conjugative carbocation reactions.

As a general description of aryl substituent effects, the Yukawa-Tsuno LArSR equation (1)3) has been used for a variety of reactions, in which a cation is developed at the conjugate site in the transition state,4–10)

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

The *r* value is a parameter characteristic of a given reaction, measuring the resonance demand, i.e., the degree of resonance interaction between the aryl and reaction site in the rate-determining transition state.3) What we have envisaged in the LArSR Eq. 1 is to introduce the concept of varying resonance demands into the substituent effect analysis.1–3,5,6a,8a,9,10) This *r* parameter permits an evaluation of the nature of the transition state, and has been widely applied to the assignment and interpretation of reaction mechanisms.3,4) However, it has been noted in the literature that the simple Hammett-Brown treatment works just as well4,11–13) and, therefore, the use of our LArSR Eq. 1 is superfluous.14) More critical analyses cast doubt on the real merit of the *r* parameter and argue against its significance as a measure of resonance demand.4,12) The critical view essentially stands on the assumption of a fixed resonance demand ($r=1$) for conjugative carbocation reactions,12) supported by the broad applicability of the σ^+ treatment.15) It appears to be necessary to reexamine whether our basic LArSR concept of varying demands on resonance effects with different systems is valid.

These critical opinions appear to arise mostly from the fact that typical benzylic solvolyses and relevant reactions generally do not give any significantly different *r* values from unity, defined for the α-cumyl (1-methyl-1-phenylethyl) solvolysis.5,16) We have already pointed out earlier that the simple Brown σ^+ treatment may be practically applicable to reactions having an *r* value within the range from 0.8—1.2.5a) While the Brown σ^+ may be applied as a good average for describing enhanced resonance effects in the ordinary solvolyses, the discrepancy of more than ±0.3 in the *r* parameter from unity must be far beyond the limit of applicability of the Brown σ^+ scale.8a) Thus, our answer to such criticism will be provided by an analysis of systems whose *r* values differ significantly from unity. In a previous paper we discussed from this point of view the substituent effect on the solvolysis of neophyl brosylates (2-methyl-2-phenylpropyl *p*-bromobenzenesulfonates)1) as a typical system giving a distinctly lower resonance demand. In benzylic solvolysis series, the solvolysis generating a more destabilized carbocation tends to have a higher resonance demand. Recently, solvolyses of benzylic systems strongly deactivated by an electronegative substituent at the α position have been studied extensively.13,17–20) Distinctly high resonance demands may be anticipated for such extremely deactivated carbocation systems. Thus, our interest was directed to such a reaction, as an appropriate system for the examination of varying resonance demands. Liu et al.13) studied the substituent effect on the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates, and found a linear LArSR correlation with a distinctly high *r* value.13b) We also determined the solvolysis rates for an extended series of substituents and analyzed the substituent effect based on the LArSR Eq. 1. The results of the correlation analysis have provided strong support for the LArSR relationship with an extremely high resonance demand for this solvolysis. Nevertheless, Liu et al. later noted that both the $\rho^+\sigma^+$ and the LArSR equations show equal predicting ability of the rates and, therefore, the σ^+ treatment is preferred because of its simplicity.13b,d) It is not their preferred use of the σ^+ treatment for simplicity that matters, but obvious conflicts in the conclusion concerning the mechanism or the nature of reaction derived therefrom. The substituent effects on the solvolyses generating extremely deactivated carbocations have been analyzed in the same way based on the simple Brown $\rho^+\sigma^+$ equation. Accordingly, a critical examination appears to be necessary concerning the substituent effect in this system, for a proper understanding of the nature of deactivated systems.

Results

The rates of solvolysis in 80 vol% aqueous ethanol (80E) were determined mostly by a conductometric procedure at a concentration of ca. 10^{-4} mol dm^{-3}. Because of the wide spread of reactivity (over 10^{12} with substituents), the rates of solvolysis of the tosylates were determined only for substituted derivatives less reactive than the *p*-phenoxy one, and the rates for more reactive derivatives than the *p*-methyl one were determined by using the corresponding bromides.

On the other hand, the solvolysis rates of more deactivated derivatives than *m*-halo ones were extremely slow to follow by the solvolysis of tosylates in 80E at appropriate temperatures. Thus, the rates of deactivated derivatives were determined using faster reacting *m*-nitrobenzenesulfonates (nosylates). The kinetic results are listed in Tables 1 and 2. The rate constants are generally in good agreement with those reported by Liu et al.[13] where comparisons are possible. The tosylate/bromide rate ratios are remarkably constant and there is a precisely linear relation (R=0.9976, SD=±0.073, and n=7) between tosylates and bromides over 10^3 in reactivity ranging from *p*-PhO to *p*-Me substituents. The linear relationship

$$\log k_{\mathrm{OTs}} = (0.941\pm0.029)\log k_{\mathrm{Br}} + 4.210 \qquad (2)$$

was utilized for an estimation of the solvolysis rates of tosylates more reactive than the *p*-phenoxy derivative. Similarly, a good linear free energy relationship (R=0.9992, SD=±0.062, and n=6) was observed between solvolyses of the tosylates and nosylates,

$$\log k_{\mathrm{OTs}} = (1.034\pm0.020)\log k_{\mathrm{ONs}} - 1.822. \qquad (3)$$

This relation also was utilized to estimate the rates of the corresponding tosylate solvolysis for several slow reacting derivatives. A complete set of relative reac-

Table 1. Rate Data of 1-Aryl-1-(trifluoromethyl)ethyl Tosylates in 80% Aq EtOH[a]

Subst.	10^5k/s^{-1} (Temp/°C)	10^5k/s^{-1} 25 °C	$\Delta H^{\ddagger}_{25\,°C}$ [b]	$\Delta S^{\ddagger}_{25\,°C}$ [b]
			kcal mol^{-1}	e.u.
4-OCH$_2$CH$_2$-3[c]		4720000[d]		
4-MeO-3-Me		1580000[d]		
p-MeO		378000[d]		
p-MeS		74900[d]		
p-PhO	44.75(−10), 196.0(0), 740.5(10)	4784[e]	20.2	3.1
4-MeO-3-Cl	139.2(0), 273.0(5)	3218[f]		
2-Fluorenyl	321.5(5)	3426	18.9	−1.8
4-MeS-3-Cl	56.00(5)	660.1	19.7	−2.3
3,4,5-Me$_3$		164.9		
3,4-Me$_2$	178.6(35), 551.0(45)	51.51[g]	21.2	−2.4
4-MeO-3-CN	502.4(45)	47.98	21.5	−1.4
p-Me	4.800(15), 218.6(45), 583.6(55)	18.95[h]	22.5	−0.3
p-Ph		13.8[i]		
4-MeS-3-CN		15.45		
2-Naph	121.7(45)	10.05	22.9	0.0
p-*t*-Bu	26.36(35), 83.91(45)	7.405	23.0	−0.6
3,5-Me$_2$	9.212(45)	0.6533	24.4	−0.6
p-F	1.638(35), 5.800(45), 18.57(55)	0.561[e]	23.8	−3.2
m-Me		0.210[i]		
H	0.3011(35), 1.152(45), 3.811(55)	0.07497[e,j]	25.0	−2.6
p-Cl		0.0456[e,k]		
p-Br	0.6235(45)	0.0353[f]		
m-F		0.000660[l]		
m-Cl		0.000448[e,k]		
m-Br		0.000337[l]		
m-CF$_3$		0.0000401[l,m]		
m-CN		0.0000174[l]		
p-CF$_3$		0.0000123[l,n]		
p-CN		0.00000515[o]		

a) Volume percent of ethanol. b) 1 cal=4.184 J. c) 1-(2,3-Dihydrobenzofuran-5-yl)-1-(trifluoromethyl)ethyl derivative. d) Calculated from linear logarithmic rate relation between tosylates and bromides (Eq. 2). e) Extrapolated from rate data at other temperatures. f) Calculated from linear logarithmic rate relation between temperatures. g) Ref. 13c, 42.3×10^{-5}s^{-1}. h) Refs. 13a and b, 17.3×10^{-5}s^{-1}; Ref. 20b, 17.0×10^{-5}s^{-1}. i) Ref. 13b. j) Refs. 13a and b, 0.0757×10^{-5}s^{-1}; Ref. 20a, 0.0865×10^{-5}s^{-1}. k) Refs. 13a and b. l) Calculated from linear logarithmic rate relation between tosylates and *m*-nitrobenzenesulfonates (Eq. 3). m) Ref. 13b, 2.57×10^{-10}s^{-1}. n) Refs. 13a and b, 1.27×10^{-10}s^{-1}. o) Calculated from linear logarithmic rate relation between tosylates in 80E and nosylates in 50% aq ethanol.[2b]

Table 2. Rate Data of 1-Aryl-1-(trifluoromethyl)ethyl Systems in 80% Aq EtOH[a]

Subst.	10^5k/s^{-1} (Temp/°C)	10^5k/s^{-1} 25 °C	$\Delta H^{\ddagger}_{25\,°\mathrm{C}}$[b]	$\Delta S^{\ddagger}_{25\,°\mathrm{C}}$[b]
			kcal mol^{-1}	e.u.
		Bromides		
4-OCH$_2$CH$_2$-3[c]		202.0		
4-MeO-3-Me	4.216(5)	63.30	21.7	−0.3
p-MeO	135.7(45)	13.81[d]	21.0	−5.7
p-MeS	28.64(45)	2.627[e]	21.9	−5.0
p-PhO	1.786(45), 10.25(60),[f] 47.65(75)	0.1399[g,h]	23.5	−6.5
4-MeO-3-Cl	1.099(45), 6.192(60), 27.82(75)	0.08989[g]	23.1	−8.6
2-Fluorenyl	1.138(45), 35.27(75)	0.07857[g]	24.6	−4.0
4-MeS-3-Cl	0.2915(45), 8.968(75)	0.02025[g]	24.5	−6.8
3,4,5-Me$_3$	0.600(65), 23.8(100)	0.00308[g]	25.8	−6.4
3,4-Me$_2$	0.2045(65), 0.655(75),[i] 8.80(100)[j]	0.000951[g,k]	26.3	−6.9
p-Me		0.00044[g,l]		
		m-Nitrobenzenesulfonates		
p-*t*-Bu	15.84(0)	578.6	22.7	7.4
3,5-Me$_2$	1.363(0)	54.21	23.3	4.5
p-F	460.3(45)	41.91	22.0	−0.2
H	95.08(45)	7.336	23.6	1.5
p-Cl	70.34(45)	5.278	23.8	1.8
m-F	1.037(45), 6.422(60), 10.94(65) 32.81(75)	0.07097[g]	24.7	−3.8
m-Cl	0.6519(45), 4.087(60), 20.53(75)	0.04489[g]	25.2	−3.2
m-Br	0.5999(45), 21.39(75)	0.0371[g]	25.6	−2.0
m-CF$_3$	0.307(55), 45.8(100)	0.00472[g]	26.5	−3.3
m-CN	0.141(55), 21.8(100)	0.00211[g]	26.7	−4.3
p-CF$_3$	0.103(55), 1.295(75), 17.0(100)	0.00151[g]	27.0	−3.8

a—c) See footnotes in Table 1. d) Refs. 13a and b, 12.9×10^{-5}s^{-1}. e) Ref. 13c, 2.13×10^{-5}s^{-1}. f) Ref. 13c, 10.6×10^{-5}s^{-1}. g) Extrapolated from rate data at other temperatures. h) Ref. 13c, 0.160×10^{-5}s^{-1}. i) Ref. 13c, 0.838×10^{-5}s^{-1}. j) Ref. 13c, 13.3×10^{-5}s^{-1}. k) Ref. 13c, 0.00123 $\times10^{-5}$s^{-1}. l) Refs. 13a and b.

tivities of the tosylate solvolysis in 80% aq. ethanol at 25 °C, including those estimated based on the above linear relations, is given in the summary in Table 1.

Substituent effect analysis has been carried out by an ordinary least-squares procedure based on Eq. 1 and the Brown $\rho^+\sigma^+$ equation. The substituent parameters, σ°, $\Delta\bar{\sigma}^{+}_{R}$, and σ^+, employed in the present analysis are mostly the standard values (Table 3). The substituent parameters for *m*,*p*-disubstituted derivatives are defined based on the combined effects of two substituents as a unified substituent.[5b,8a] It is often pointed out that the substituent parameters are subject to change with the solvent.[21] The solvent modification of substituents in an 80E solution is, in fact, not so significant that it requires any serious correction of the substituent parameters for most substituents. However, any serious effect of the deviation of a few particular substituents on the correlation results should be avoided in the present critical examination of the LArSR analysis. Accordingly, the parameter values were slightly modified for several substituents in order to achieve precise conformity to Eq. 1 within ±0.02 σ-unit; the parameter values in Table 3 will be most appropriately applicable to reactivities in an aqueous ethanolic solution. The most important correction employed in the present analysis is the correction of 0.03—0.04 σ unit for the resonance parameters of all the *p*-MeS derivatives, whereas no

Table 3. Substituent Constants Used for Correlation Analysis

Subst.	σ^0	$\Delta\bar{\sigma}^{+}_{R}$	σ^+
4-OCH$_2$CH$_2$-3	−0.19	−0.75	−0.95
4-MeO-3-Me	−0.18	−0.70	−0.88
p-MeO	−0.10	−0.70	−0.80
p-MeS	0.065	−0.72	−0.61
p-PhO	0.063	−0.59	−0.53
4-MeO-3-Cl	0.22	−0.69	−0.47
2-Fluorenyl	−0.02	−0.49	−0.51
4-MeS-3-Cl	0.40	−0.73	−0.33
3,4,5-Me$_3$	−0.262	−0.187	−0.45
3,4-Me$_2$	−0.193	−0.187	−0.38
4-MeO-3-CN	0.52	−0.69	−0.17
p-Me	−0.124	−0.187	−0.311
p-*t*-Bu	−0.155	−0.100	−0.255
p-Ph	0.039	−0.26	−0.22
4-MeS-3-CN	0.66	−0.73	−0.07
3,5-Me$_2$	−0.138	0.000	0.138
p-F	0.20	−0.24	−0.06
m-Me	−0.069	0.000	−0.069
H	0.000	0.000	0.000
p-Cl	0.27	−0.166	0.115
p-Br	0.27	−0.146	0.15
m-F	0.337	0.000	0.352
m-Cl	0.373	0.000	0.399
m-Br	0.391	0.000	0.405
m-CF$_3$	0.53	0.000	0.52
m-CN	0.60	0.000	0.562
p-CF$_3$	0.62	0.000	0.612
p-CN	0.67	0.000	0.659

Table 4. Correlation Analysis for 1-Aryl-1-(trifluoromethyl)ethyl Tosylate

No.	Substituent set	Correlation	n	ρ	r	SD	R
1.	All subst.	LArSR	28	−6.287	1.388	0.070	0.9998
		σ^+	28	−7.535		0.493	0.9903
2.	Electron-donors[a)]	LArSR	21	−6.291	1.389	0.072	0.9996
		σ^+	21	−7.792		0.563	0.9750
3.	Without disubst[b)]	LArSR	23	−6.269	1.397	0.075	0.9998
		σ^+	23	−7.501		0.353	0.9956
4.	Limited Electron-donors.[c)]	LArSR	13	−6.207	1.407	0.072	0.9997
		σ^+	13	−8.376		0.307	0.9943
5.	Liu[d)]	LArSR	12	−6.199	1.411	0.077	0.9998
		σ^+	12	−7.530		0.399	0.9939
6.	Less reactive than *p*-PhO	LArSR	24	−6.303	1.388	0.071	0.9997
		σ^+	24	−7.409		0.525	0.9839
7.	Bromide set[e)]	LArSR	11	−6.536	1.424	0.085	0.9992
		σ^+	11	−8.330		0.551	0.9623
8.	*m*-Correlation[f)]	σ^0	10	−6.241	—	0.064	0.9994

a) More reactive substrates than H. b) No disubstituted compounds involved. c) Electron-donors of common use; 4-OCH$_2$CH$_2$-3, 4-MeO-3-Me, *p*-MeO, *p*-MeS, *p*-PhO, 3,4-Me$_2$, *p*-Me, *p*-Ph, *p*-*t*-Bu, 3,5-Me$_2$, *p*-F, *m*-Me, and H. d) Liu's data set (Ref. 13); *p*-MeO, *p*-MeS, *p*-PhO, 3,4-Me$_2$, *p*-Me, *p*-Ph, *m*-Me, H, *p*-Cl, *m*-Cl, *m*-CF$_3$, and *p*-CF$_3$. e) Leaving bromide system. f) Meta and π-accepting para substituents.

correction was required for the corresponding *p*-MeO derivatives. The nonlinear dependence of the resonance effect of *p*-MeS substituent upon the reactions has frequently been noticed.[22)] Further details will be discussed elsewhere.

The results of the correlation analysis are summarized in Table 4. Meta and π-accepting para substituents satisfy precisely a linear Hammett relationship against either σ^+ or σ^0, and the ρ_m value remains essentially the same for the solvolysis of tosylates and nosylates in 80% aqueous ethanol. The LArSR ρ values are all identical to the ρ_m value, whereas ρ^+ values based on the σ^+ correlation differ significantly from the ρ_m value. The entire substituents set satisfies the LArSR Eq. 1 with high precision, with a standard deviation of 0.070 and a correlation coefficient of 0.9998. Exactly the same LArSR correlation is obtained for set No. 6, excluding more reactive substituents than the *p*-MeS group, of which the rates are based on the solvolysis of the corresponding bromides. This suggests that the extrapolation of the rates for extremely high reactive derivatives based on bromide solvolysis is never the cause of the deviation of r from unity. Set No. 5 on which Liu's analysis was based gives an identical LArSR correlation with a precision comparable to that of the all substituents set (No. 1). It should be noted that the bromide set (No. 7) consisting only of highly reactive substituents gives a good correlation with comparable precision, but with a slightly different r value (discussed further below). For any substituent sets, irrespective of the number and nature of constituting substituents, the LArSR correlations are all excellent and distinctly better by one order of magnitude in SD than the corresponding σ^+ correlations.

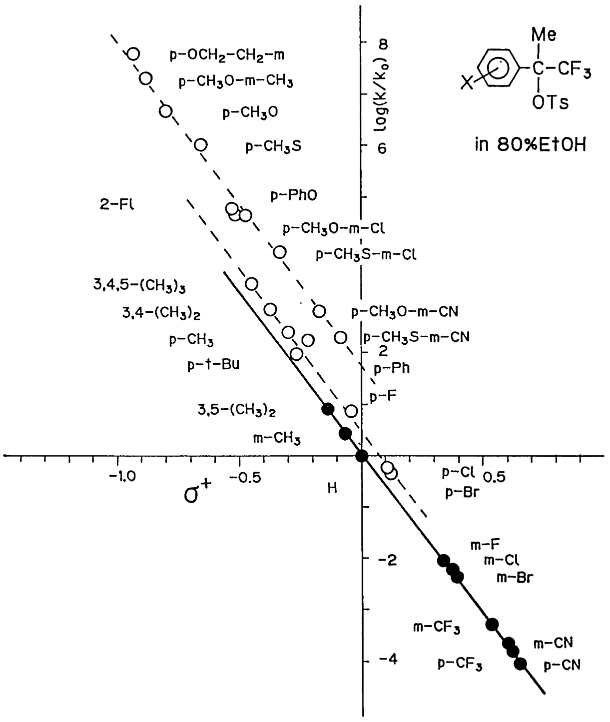

Fig. 1. The σ^+ plot for solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates in 80% aq EtOH at 25 °C.

Discussion

Despite Liu's suggestion of a good σ^+ correlation,[13b)] the σ^+ plot in Fig. 1 appears to be only fair, or even poor. Meta and π-accepting para substituents construct a good linear relationship, the range of which (about 10^5 in reactivity) is wide enough to define the ρ_m value. On the other hand, *p*-π-donor substituents exhibit a wide dispersion pattern, but the deviations are apparently systematic in that they all deviate in the direction of activation from the meta line and in proportion to their resonance strengths. The plot apparently splits into separate lines for strong π-donors (RO and RS groups), and for weak π-donors (alkyls and halogens), one each running parallel to the *m*-line with significant gaps. The gap of ca. 2 log-unit between lines seems to be too large to be attributed to experimental error. The $\rho^+\sigma^+$ treatment obviously fails to give a single linear correlation, or even a single monotonically curved one for all classes of substituents.

The excellent linear LArSR plot (squares in Fig. 2) with an *r* value of 1.39 contrasts sharply with the poor linear plot given by σ^+ (open circles in Fig. 2). Figure 2 clearly accounts for the significance of *r* in the LArSR description of resonance effects as well as the way the substituent constant changes with a change in the resonance demand. The meta correlation based on resonance-insensitive substituents should be a rigid reference common to both the σ^+ and LArSR analyses; its excellent linearity provides convincing evidence for the absence of a mechanistic change over the range covered by these substituents. *p*-π-Donor substituents in the σ^+ plot all deviate toward enhanced reactivity from the meta correlation line, suggesting an enhanced resonance demand of this system. The horizontal line segments between σ^+ and σ° for para π-donor substituents correspond to their resonance capabilities, i.e., $\Delta\bar{\sigma}_R^+$ values. The LArSR correlation corresponds to the line which divides all of the resonance segments of para π-donors at a constant external ratio referred to the *r* value of 1.39. Clearly, it can be seen that only with this unique *r* value do para π-donor substituents all coalesce into a single straight line including meta and π-accepting para substituents. This graphical interpretation is confirmed by the results of the statistical LArSR analysis given in Table 4. From the accuracy of the overall fit, the simple Brown σ^+ correlation is not compatible with the LArSR one.

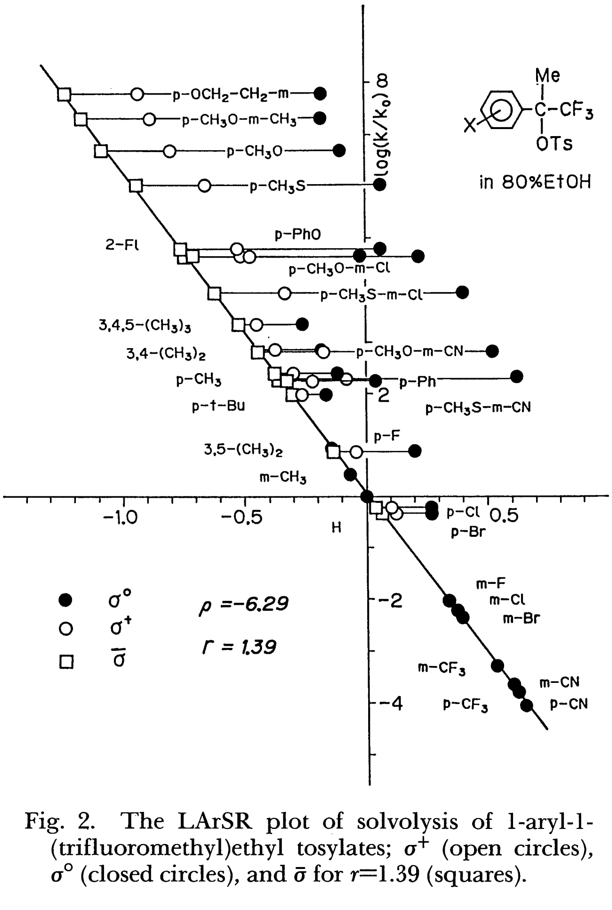

Fig. 2. The LArSR plot of solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates; σ^+ (open circles), σ° (closed circles), and $\bar{\sigma}$ for r=1.39 (squares).

Liu et al.[13b)] gave a ρ^+ value of -7.46 for their data set (or a better-fit ρ^+ of -6.85 excluding *p*-MeO group) by the Brown σ^+ analysis; nevertheless, they later reported a good σ^+ relation with an extremely high ρ^+ value of -10 for a limited range of electron-donating derivatives,[13c)] which is clearly different from the ρ_m value based upon deactivating substituents. A linear relationship, in principle, indicates a constant mechanism over the range of substituents involved, whereas a curve break of the relationship is indicative of a change in the mechanism. In contrast with the completely linear LArSR correlation for the present solvolysis, the nonlinear Brown σ^+ correlation with different ρ^+ values for the activated and deactivated regions is just what would be expected for a mechanistic shift with a substituent change, as observed in benzyl solvolysis.[23)] It is rather serious that both equations lead to conflicting conclusions regarding the mechanism from the same solvolysis data set. Although a k_c-k_s mechanistic transition might perhaps be the cause of the nonlinear σ^+ plot for this highly deactivated system, the ρ^+ value of -6.4 for the electron-acceptor region of substituent is clearly too high to be accounted for by the k_s mechanism,[13a)] and the relevant experimental evidence all argues for the k_c mechanism for the entire range of substituents.[13b,20)] Liu et al. therefore came to claim that the ρ value for the bromide solvolysis had to be much higher than that for the tosylate solvolysis.[13c)] However, this argument has also been incompatible with the present precise linear relationship between the solvolyses of bromides and tosylates with an essentially unit slope. More crucial is the fact that the σ^+ treatment gives neither a linear nor a single smooth-curved plot but, rather, a significantly scattered pattern. The mechanistic transition, itself, should depend in a simple manner upon substituent polarities, and will give a single, continuous, smooth-curved correlation with a suitable substituent constant scale. The basic requirement for the interpretation of the curve break in terms of a mechanistic change should therefore be a continuous concave plot for the substituent effect correlation. Any discontinuous split pattern of the σ^+ plot should in principle be incompatible with a simple k_c-k_s mechanistic transition. These inconsistencies must arise merely from the intrinsic deficiency of any single-parameter treatment.

The present solvolysis is a typical system proceeding via an extremely electron-deficient cationic transition state, which may reflect its extremely high resonance demand. Further a detailed consideration should be required for the substituent effect behavior, especially concerning the accuracies of the LArSR and Brown correlations, and the real reliability of the r value.

The validity of the LArSR correlation can be most clearly accounted for by the plot in Fig. 3, which displays the dependence of the standard deviations on r in the least-squares fitting to Eq. 1, without constraint for the ρ value. Curve 1 shows the change of SD as a function of r for the set (refers to set No. 1 in Table 4) involving all substituents. The SD changes remarkably with the r value, giving a sharp wedge-shape plot; even a minor deviation from the best-fit r causes a sharp increase in the SD value. This is, indeed, a schematic illustration of the converging process in the iterative least-squares calculation procedure. The depth and steepness of the wedge may be indicative of a significant convergency to the best-fit r point as well as the real validity of this LArSR correlation. While the sufficient depth should be a basic requirement for acceptable conformity, the steepness is a more direct measure of the reliability of the r value and, therefore, will be of particular importance in discussing varying resonance demands. An identical SD vs. r plot (curve 2) of significant convergence at the same best-fit r value can also be obtained for set No. 2, excluding electron-acceptor substituents. The small change in depth may simply be due to a change in the number of substituents. The σ^+ correlation appears to be as equally less accurate for this set as the all substituents set. This fact strongly argues against any acceptable σ^+ correlation suggested so far for the electron-donative region of a bisected bilinear correlation. On the other hand, Liu's set (Set No. 5) gives an accurate best-fit LArSR correlation, but an appreciably broader SD vs. r plot of low convergency (curve 5). The broadness becomes more significant when the acceptor substituents are excluded from set No. 3 for typical substituents of ordinary use, given by curve 4 for set No. 4. A minor drift of the best-fit r value in these sets (see Table 4) has no statistical significance, because of the essentially flat basin of the SD vs. r plot. While the steepness depends appreciably upon the combination of constituting substituents in the set, the depth constantly achieves a sufficiently low value and, hence, detailed consideration of the subtle change in the SD value below the acceptable conformity level does not appear to be very meaningful.

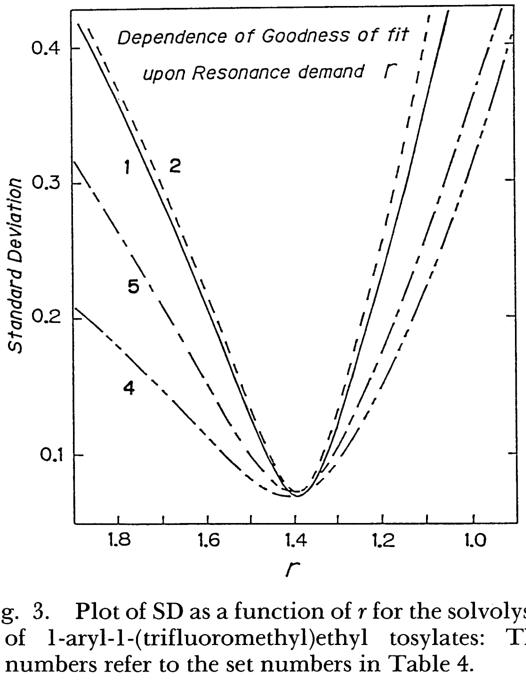

Fig. 3. Plot of SD as a function of r for the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates: The numbers refer to the set numbers in Table 4.

Practically, the reliability of the r value of this system may be evaluated in terms of the width of the SD vs. r plot at such a level of SD=±0.10 as a reference for acceptable conformity to Eq. 1. Thus, the r value defined by the all substituents set may be valid within a possible uncertainty of the order of ±0.06. For Liu's set a relatively lower validity of the order of ±0.10 in this criterion will have to be estimated for its r value. The magnitudes of these reliability parameters are two or three times as large as the ordinary statistical indices. Even if such a large possible uncertainty of ±0.1 may be allowed in the r value, this system having an r value of 1.39 should be far out of the range of applicability of the σ^+ scale. The result of the validity analysis of r argues strongly against Liu's conclusion that the Brown σ^+ treatment can be equally applied to this system.

In Fig. 3, we can observe a clear difference in the steepness of SD vs. r curves between two series of substituent sets, Nos. 1—2 and Nos. 4—5. The convergency to the best-fit correlation depends upon the combination of substituents. The LArSR correlation analysis basically requires nonlinearity (or randomness) between σ° and $\Delta\bar{\sigma}_R^+$ parameters. Especially, for distinguishing between the LArSR and Brown σ^+ analyses, the basic requirement of nonlinearity between σ^+ and $\Delta\bar{\sigma}_R^+$ for π-donor substituents should be considered severely. The relation between σ^+ and $\Delta\bar{\sigma}_R^+$ is shown in Fig. 4. Typical π-donor substituents of common use (given by closed circles) fall close to a straight line given by the equation $\Delta\bar{\sigma}_R^+ = (0.70\pm0.05)\,\sigma^+ - 0.08$ (n=9, R=0.981, and SD=±0.09). For these substituents, we may find a rough Brown $\rho^+\sigma^+$ correlation, as

$$\log k/k_0 = \rho(0.70r+0.30)\sigma^+.$$

It follows, as a crude approximation, that

$$\log k/k_0 \doteqdot \rho r \sigma^+.$$

The electron-donor substituents of common use will always give a linear plot against σ^+, irrespective of the

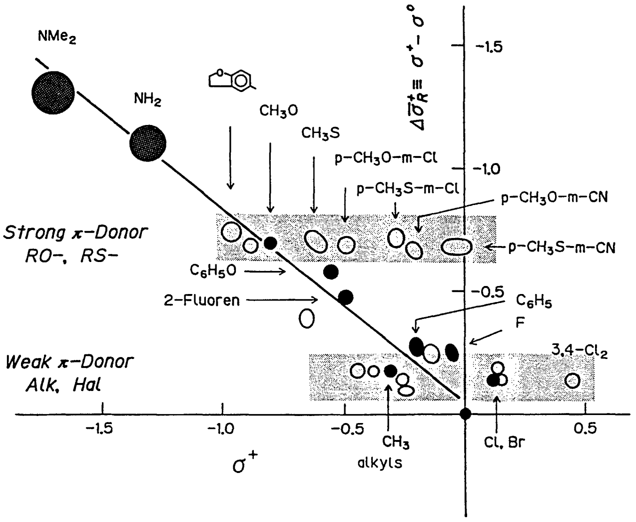

Fig. 4. Plot of $\Delta\bar{\sigma}_R^+$ values against σ^+.

r value, with a slope different from the ρ_m value. This is just what was observed for Liu's analysis; the σ^+ correlation giving an extremely high ρ^+ value for electron-donor and a ρ^+ value of ordinary size for electron-acceptor region should inevitably suggest an unlikely mechanistic shift for this reaction.

The LArSR correlation for any set consisting only of these ordinary substituents is generally excellent, but the precision of the correlation is not quite sensitive to the change in the r value, and meta substituents capable of giving a reliable ρ value should be required for accurately determining the r value for such a system. In practical applications, a combination of different classes of π-donors is essential for any precise LArSR analysis, and strong π-donor substituents of less negative σ^+ values are particularly important for an accurate estimation of the r value. Provided the sufficient randomness between the σ^+ and $\Delta\bar{\sigma}_R^+$ values, the para π-donor substituents, themselves, must have a potential self-convergency to an LArSR correlation with unique r and ρ values characteristic of the system.

Experimental

Materials: Most of α,α,α-trifluoroacetophenones were synthesized according to Stewart's procedure of Grignard reaction of substituted bromobenzenes with trifluoro-

Table 5. Physical Data of 1-Aryl-1-(trifluoromethyl)ethyl Arenesulfonates

Subst.	Mp/°C	Carbon/%		Hydrogen/%		Nitrogen/%	
		Found	Calcd	Found	Calcd	Found	Calcd
Tosylates[a]							
4-MeS-3-Cl	47.0—48.0	48.11	48.06	3.80	3.80		
3,4,5-Me3	63—64(decomp)	59.18	59.06	5.53	5.48		
3,4-Me2	72.0—73.0	58.04	58.06	5.11	5.14		
4-MeO-3-CN	98.0—100.0	54.11	54.13	4.22	4.26	3.41	3.51
p-Me	73.2—73.9[b]	57.02	56.98	4.85	4.78		
p-*t*-Bu	69.0—72.0	60.08	59.99	5.84	5.79		
4-MeS-3-CN	110.0—111.0	51.75	51.91	3.95	4.11	3.86	3.36
3,5-Me2	82.0—83.0	58.09	58.06	5.23	5.14		
m-Me	76.5—77.5[c]	57.00	56.98	4.86	4.78		
p-F	70.2—70.8	53.11	53.04	3.93	3.89		
H	104.5—105.5[d]	55.78	55.81	4.38	4.39		
p-Cl	92.5—93.2[e]	50.89	50.74	3.74	3.73		
p-Br	110.8—112.1	45.56	45.40	3.51	3.33		
m-F	87.8—88.3	53.27	53.04	4.02	3.89		
m-Cl	81.5—82.8[f]	50.71	50.74	3.80	3.73		
m-Br	88.0—88.5	45.73	45.40	3.39	3.33		
m-Nitrobenzenesulfonates[g]							
3,5-Me2	58.0—59.8	50.32	50.62	4.00	4.00	3.47	3.47
p-F	73.5—74.0	45.88	45.81	2.89	2.82	3.52	3.56
H	80.0—81.5	48.11	48.00	3.31	3.22	3.62	3.73
p-Cl	87.0—88.5	44.19	43.97	2.72	2.71	3.43	3.42
m-F	72.0—73.0	46.04	45.81	2.88	2.82	3.70	3.56
m-Cl	59.0—59.7	44.12	43.97	2.88	2.71	3.70	3.42
m-Br	77.0—78.5	40.03	39.66	2.52	2.44	3.10	3.08
m-CF3	74.5—75.5	43.30	43.35	2.52	2.50	3.30	3.16
m-CN	82.0—83.0	48.06	48.00	2.79	2.77	6.99	7.00
p-CF3	96.0—96.5	43.37	43.35	2.49	2.50	3.30	3.16
p-CN	127.7—128.5	47.93	48.00	2.79	2.77	7.00	7.00

a) *p*-PhO (mp 88—89 °C), 4-MeO-3-Cl (mp 76 °C, decomp), and 2-Fluorenyl (mp 64—65 °C, decomp) derivatives were too unstable to give accurate elemental analysis result. b) Lit,[13b)] mp 73 °C. c) Lit,[13b)] mp 75.5—76.5 °C. d) Lit,[13b)] mp 103.5 °C; 101 °C.[20a)] e) Lit,[13b)] mp 93.0—93.5 °C. f) Lit,[13b)] mp 81.5 °C. g) *p*-*t*-Bu derivative (mp 43 °C, decomp) was not sufficiently stable to give accurate elemental analysis result.

acetic anhydride at −78 °C in Dry Ice-acetone bath.[24] 2-Trifluoroacetylfluorene (mp 81.5—83.5 °C) and 3-bromo-4-methylthio-*α,α,α*-trifluoroacetophenone were prepared by the Friedel-Crafts reaction of the corresponding aromatics with trifluoroacetic anhydride. 3-Bromo-4-methoxy-*α,α,α*-trifluoroacetophenone was obtained by the bromination of *p*-methoxy-*α,α,α*-trifluoroacetophenone in acetic acid at 50 °C.

Substituted trifluoroacetophenones were converted into the corresponding 1-aryl-1-(trifluoromethyl)ethanols by the Grignard reaction with methylmagnesium iodide. The alcohols obtained were purified by column chromatography on silica gel. Tertiary alcohols were also prepared by Grignard reactions of the appropriate arylmagnesium bromide with 1,1,1-trifluoroacetone.[13b] An ethereal solution of 1,1,1-trifluoroacetone was added dropwise to the Grignard solution of an arylmagnesium bromide in ether at ice-bath temperature. 4-MeO-3-CN, 4-MeS-3-CN, *p*-CN, and *m*-CN substituted tertiary alcohols were prepared by the reaction of the corresponding bromo derivatives with copper(I) cyanide in DMF by the Friedman-Shechter method.[25]

1-Aryl-1-(trifluoromethyl)ethyl arenesulfonates were synthesized according to Tidwell's method.[20a] 0.026 mol of tertiary alcohol in 25 cm^3 of ether was added to 0.06 mol of NaH in 50 cm^3 of ether at room temperature under nitrogen atmosphere. The mixture was stirred for 1 h; then, 0.025 mol of *p*-toluenesulfonyl chloride or *m*-nitrobenzenesulfonyl chloride in 75 cm^3 of ether was added dropwise. After stirring overnight, the mixture was filtered and the filtrate was concentrated under vacuum to give solid tosylate or nosylate, and purified by recrystallization from ether-hexane. Physical constants and analytical data are summarized in Table 5.

1-Aryl-1-(trifluoromethyl)ethyl bromides were prepared according to Liu's method.[13b,c] Phosphorus tribromide, 8 mmol was added slowly to 7 mmol of alcohol with stirring in an ice bath. After stirring at 40—50 °C for 4 h, the reaction mixture was poured into ice-water, extracted with ether and washed with Na_2CO_3 solution and sat. NaCl solution. The bromide was purified through column chromatography on alumina. Most of the bromides were not solidified, except for 2-Fluorenyl, mp 103—106 °C, which were stored in a freezer. 4-OCH_2CH_2-3 and 4-MeO-3-Me substituted bromides were prepared by the bromination of the alcohols with HBr gas; HBr gas was passed into the ethereal solution of alcohol in the presence of anhydrous $CaCl_2$ with stirring for 3 h, filtered, and concentrated under vacuum. The residue was diluted with ether, treated with fresh anhydrous $CaCl_2$ and evaporated in vacuo. This procedure was repeated several times until the complete removal of excess HBr gas. The residue was directly utilized for kinetic measurements.

Solvents: Commercial 95% ethanol was dehydrated twice by heating under reflux with magnesium ethoxide and distilled. Deionized water was refluxed with $KMnO_4$ and the distillate was redistilled immediately before use. 80% aqueous ethanol (80E) was prepared by mixing corresponding volumes of ethanol (80) and water (20) at 25 °C.

Kinetic Measurement: Solvolysis rates were measured by conductometric method.[26] Conductance measurements were made in a cell with bright platinum electrodes using approximately a 25 or 50 cm^3 solution at an initial concentration of 10^{-4} mol dm^{-1} of a substrate ester. Conductivity readings were taken by using a conductivity meter (CM-50AT equipped with time interval unit and printer, TOA Electric Ltd.). Solvolyses were followed by taking at least 50 points at appropriate intervals for 2.5 half-lives and an infinity reading was taken after 10 half-lives. For the conductivity measurement of relatively fast reactive substrates, complete solutions can be attained relatively quickly by dissolving the substrates in a small amount of ethanol into 80E involving an adjustable amount of water.

The first-order rate constants were determined by a least-squares computer program; the precision of the fit to first-order kinetics was generally satisfactory over 2.5 half-lives, with a correlation coefficient$>$0.99999.

The rates of solvolysis for less reactive substrates at a higher temperature were followed by using the ampoule technique with conductivity determination. The 10^{-4} mol dm^{-3} solution was made up and sealed in twenty (5 ml) ampoules for one run. The ampoules were allowed to react in thermostated bath and the reaction was stopped by withdrawing an ampoule and immersing it in ice-water at appropriate intervals for 2 half-lives. Several ampoules were allowed to react for 10 half-lives at higher temperature 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.

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