Substituent Effects. 22.[1] The Solvolysis of α-*t*-Butylbenzyl Tosylates[2]

Yutaka TSUJI,† Mizue FUJIO, and Yuho TSUNO*
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka 812
†Laboratory of Chemistry, College of General Education, Kyushu University, Ropponmatsu, Fukuoka 810
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The rates of solvolysis of α-*t*-butylbenzyl tosylates were determined in 80% aqueous acetone (80A) and 80% aqueous ethanol (80E) for an extended series of substituents. The substituent effect can be linearly correlated in terms of the Yukawa–Tsuno LArSR relationship, with a ρ value of −5.542 and an r value of 1.093 in 80A, and −5.650 and 1.106 in 80E, respectively. The large negative ρ and exalted r values suggest the operation of the k_c mechanism in this solvolysis without nucleophilic solvent assistance and methyl participation. From a comparison of the substituent effects, the exalted r value of 1.15 observed in the solvolysis of α-methylbenzyl chlorides can be attributed to the enhanced resonance demand characteristic of secondary benzylic system rather than to a correlational artifact arising from nonlinearity due to S_N1–S_N2 mechanistic change. The solvolysis of this system can be utilized as an appropriate reference system for the accurate estimation of σ^+ constants in various solvents.

The Yukawa–Tsuno LArSR equation[3] accounting for the variable resonance effect has been widely used for the analysis of substituent effects on the solvolyses generating a conjugative carbocation,[1,4–8]

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

where the resonance demand parameter r value is taken to be reference standard r=1.00 (by definition) for the solvolysis of α-cumyl chlorides (1-methyl-1-phenylethyl chlorides). In the simple Brown equation,

$$\log (k/k_0) = \rho^+\sigma^+, \quad (2)$$

σ^+ appears to be the best average to fit most cases and practically applicable within satisfactory precision to the electrophilic conjugative reactions having r value in the range 0.8 to 1.2,[4a] while a definite set of σ^+ can not describe the substituent effect in the reaction having the r value outside of this range.[5–7] The r parameter in Eq. 1 has been verified to be a useful measure of the degree of resonance contribution from substituents in the rate-determining transition state, and is applicable to the estimation of the electronic structure of transition states. In the α-substituted benzylic series, the resonance demand of the solvolyses was found to be parallel to the stabilities of the parent benzylic cations.[6,7] We already reported earlier that the substituent effects on the solvolysis of α-methylbenzyl chlorides was described with excellent precision in terms of an appreciably enhanced resonance demand r value of r=1.15.[4a,b] It has been noted, however, that most systems favored by the LArSR treatment are secondary substrates in nucleophilic solvents, and such systems may also be subject to nucleophilic solvent participation.[9] In secondary benzylic solvolyses, solvent participation might become important as the substituent becomes more electron attracting, to give a monotonically concave σ^+ plot. It has thus often been noted in the literature that the higher r value observed in such a case will be less reliable.[8,10]

In order to confirm the intrinsic resonance demand of secondary benzylic solvolysis, the system to be studied should be a secondary benzylic one completely free from concurrent S_N2 mechanism. We have chosen for the present study the solvolysis of α-*t*-butylbenzyl tosylates in which the solvent nucleophilic assistance is structurally prevented, owing to the neopentyl structure of the reaction center.[11]

The solvolysis rates of α-cumyl chlorides are too fast, even in 90% aq acetone, and the rates of strongly activated substrates, especially those of *p*-MeO and *p*-MeS derivatives, were hardly determined accurately.[12] It therefore appears necessary to redetermine the σ^+ values for highly activating substituent groups. The α-*t*-butylbenzyl system shows a rate retardation by 10^3 compared with α-methylbenzyl system,[13] and is convenient for an accurate determination of the solvolysis rate, especially for activating substituents in most ordinary solvents. The solvolysis rates of a wide series of *m*-and *p*-substituted α-*t*-butylbenzyl tosylates have been determined, and the substituent effect has been analyzed based on the LArSR Eq. 1, and a reexamination of σ^+ values has been carried out in the present system.

Results

The solvolysis rates of α-*t*-butylbenzyl tosylates in 80% (v/v) aqueous acetone (80A) for an extended set of substituents were conductometrically determined at initial ester concentrations of 10^{-4}—10^{-5} mol dm^{-3}. The rate constants from repeated runs were reproducible within an accuracy of 1.5% and are summarized in Table 1 together with the activation parameters. For the extremely reactive *p*-MeO derivative the rate was unable to follow directly in 80A by our method at the ordinary temperature. The rate of this derivative in 80A at 25 °C was estimated from the rate in 90A at 0 °C, using a linear logarithmic rates relation between

Table 1. Solvolysis Rates of α-*t*-Butylbenzyl Tosylates in 80% aq Acetone

Subst.	Temp/°C	$10^5\ k/s^{-1}$		$\Delta H^{\neq}_{25\,°C}$[a]	$\Delta S^{\neq}_{25\,°C}$[a]
				kcal mol^{-1}	e.u.
p-MeO	0	1210[b]			
	25	94600[c]			
p-MeS	0	262.5,	52.99[b]		
	25	1011,[b]	5592[d]		
p-PhO	25	1760			
4-MeO-3-Cl	25	1180			
4-MeO-3-Br	0	51.78			
	25	1130		19.4	−2.4
2-Fluorenyl	25	1100			
3,4-Me_2	0	6.339,	1.001[b]		
	25	186.7		21.3	0.4
4-MeS-3-Cl	25	105.0			
p-Me	0	3.224,	0.4644[b]		
	25	95.07		21.3	−0.9
4-MeO-3-CN	0	1.784			
	25	53.20		21.4	−1.8
p-*t*-Bu	0	1.102			
	25	39.16		22.5	1.4
p-Ph	25	22.37			
β-Naph	25	18.65			
3,5-Me_2	25	6.023			
4-MeS-3-CN	25	5.335			
p-F	0	0.01432[b,e]			
	25	3.835,	0.5650[b]		
	45	7.053[b]			
m-Me	25	2.862			
H	25	1.420		24.0	−0.3
	45	19.26			
m-MeO	25	0.6096			
4-Me-3-Cl	25	0.3847			
p-Cl	25	0.378[c]		24.3	−1.9
	45	5.293			
	65	54.24			
p-Br	25	0.252[c]		24.6	−1.8
	45	3.631			
	65	38.20			
m-MeS	25	0.1673			
m-F	25	0.0138[c]		26.1	−2.3
	45	0.2344			
	75	8.957			
m-Cl	25	0.00691[c]		26.8	−1.5
	45	0.1261			
	75	5.260			
m-Br	25	0.00659[c]		26.4	−2.8
	45	0.1159			
	75	4.606			
3,4-Cl_2	25	0.00483[c]		26.7	−2.4
	45	0.08750			
	75	3.619			
m-CF_3	25	0.00119[c]		27.3	−3.1
	55	0.08820			
	100	15.43			
m-CN	25	0.000720[c]		27.1	−4.8
	60	0.09849			
	100	8.785			
p-CF_3	25	0.000434[f]			
m-NO_2	25	0.000295[f]			
p-CN	25	0.000242[f]			
p-SO_2Me	25	0.000189[f]			
3,5-Cl_2	25	0.0000983[f]			

a) 1 cal=4.184 J. b) In 90A. c) Calculated from logarithmic relation between 80A at 25 °C and 90A at 0 °C (see text). d) Estimated by log k–log k relation between 0 °C and 25 °C. e) Extrapolated from rate constants at other temperatures. f) Calculated by logarithmic correlation between tosylates and *m*-nitrobenzenesulfonates at 25 °C (see text).

90A (0 °C) and 80A (25 °C).

$$\log k_{80A}(25\,^{\circ}C) = 0.8857 \log k_{90A}(0\,^{\circ}C) + 1.674$$

($R = 0.9997$, SD $= \pm 0.038$, and $n = 4$)

On the other hand, the rates of strongly deactivating derivatives were too slow to be obtained directly by means of ordinary conductivity measurement. To avoid relatively less reliable extrapolation from higher temperatures, the rates of these substrates were determined using the *m*-nitrobenzenesulfonates which were solvolyzed about fifty times as fast as the corresponding tosylates. Rate data for *m*-nitrobenzenesulfonates are listed in Table 2. A good linear logarithmic rates relationship exists between solvolyses of the tosylates and *m*-nitrobenzenesulfonates at 25 °C over a wide range of substituents from *p*-*t*-Bu to *m*-CN,

$$\log k_{OTs} = 1.051 \log k_{ONs} - 1.508$$
($R = 0.9998$, SD $= \pm 0.041$, $n = 5$)

Rate constants for the tosylate solvolysis were estimated from the rates of *m*-nitrobenzenesulfonates using this relation and are also included in Table 1.

Solvolysis rates in 80% (v/v) aq ethanol (80E) were determined in a similar way. A direct rate determination by tosylate solvolysis was made only for less reactive derivatives than the *p*-phenoxy derivative in this faster solvolyzing solvent. The rates of faster reacting substrates were followed by the chloride solvolysis and the relative tosylate reactivities were calculated from

$$\log k_{OTs} = 0.945 \log k_{Cl} + 3.508.$$

On the other hand, rates for deactivated substrates were estimated likewise from the rates of solvolyses of corresponding *m*-nitrobenzenesulfonates. Rate data are summarized in Tables 3, 4, and 5.

Figure 1 shows the logarithmic plot of solvolysis rates of *α*-*t*-butylbenzyl tosylates in 80E against those in 80A, giving a slope of 1.024 (R=0.9994, SD=±0.087, and n=33). The precise linear relationship with a unit slope strongly indicates essential identity of substituent effect on the solvolysis in both solvents.

The LArSR Eq. 1 has been applied statistically to this system, and for a comparison, the Brown $\rho^+\sigma^+$ equation has also been applied. The results of statistical analysis are summarized in Table 6. The substituent parameters employed primarily in this analysis are mostly the standard values taken from our previous papers.[4a,b,5b]

Table 2. Solvolysis Rates of *α*-*t*-Butylbenzyl *m*-Nitrobenzenesulfonates in 80% aq Acetone

Subst.	Temp/°C	$10^5\,k/s^{-1}$	$\Delta H^{\neq}_{25\,°C}$	$\Delta S^{\neq}_{25\,°C}$
p-*t*-Bu	0	51.73		
	25	1454	21.0	3.5
m-Me	25	132.2		
H	25	69.06		
m-Cl	25	0.4584		
m-CN	25	0.04417[a]	26.9	2.5
	45	0.8137		
	65	10.62		
p-CF_3	25	0.02989[a]	27.0	2.0
	45	0.5555		
	75	23.72		
m-NO_2	25	0.02069[a]	26.8	0.7
	45	0.3770		
	75	15.69		
p-CN	25	0.01712[a]	27.4	2.4
	45	0.3334		
	75	15.11		
p-SO_2Me	25	0.01355[a]	27.9	3.8
	45	0.2797		
	75	13.67		
3,5-Cl_2	25	0.007269[a]	28.1	2.9
	45	0.1521		
	75	7.561		

a) Extrapolated from rate constants at other temperatures.

Discussion

From the above results, the substituent effects may be considered to be essentially identical in both 80A and 80E solvents. Of course solvent modification is evidently important for some particular substituents; this point will be considered separately below.

Solvolysis in 80A gives an excellent linear LArSR

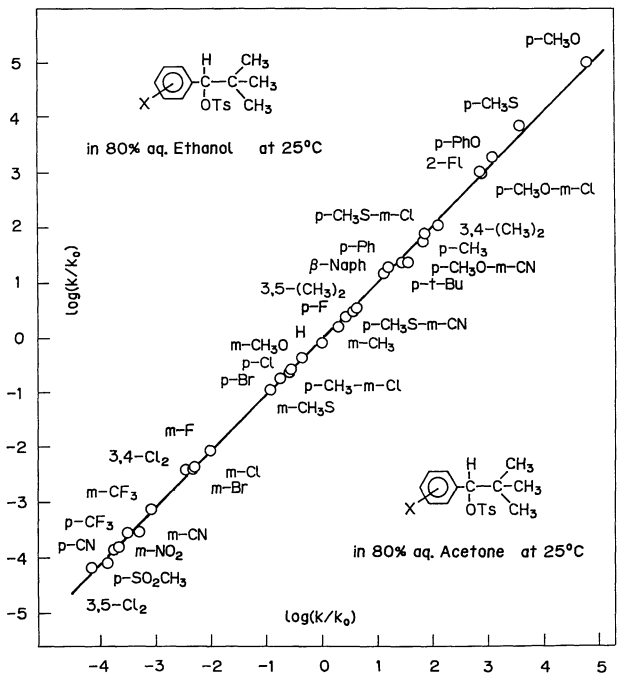

Fig. 1. Linear logarithmic rates plot between solvolyses in 80E and 80A.

Table 3. Solvolysis Rates of α-*t*-Butylbenzyl Tosylates in 80% aq Ethanol

Subst.	Temp./°C	$10^5\ k/s^{-1}$	$\Delta H^{\neq}_{25\,°C}$ / kcal mol^{-1}	$\Delta S^{\neq}_{25\,°C}$ / e.u.
p-MeO	25	1568000[a]		
p-MeS	25	104500[a]		
p-PhO	0	1211		
	25	28290[b]		
4-MeO-3-Cl	0	603.3		
	25	14660[b]		
2-Fluorenyl	0	612.0		
	25	14860[b]		
3,4-Me_2	0	62.00		
	25	1715[b]		
4-MeS-3-Cl	0	49.16		
	25	1193	20.1	−0.1
p-Me	0	31.26		
	25	862.9	20.9	2.1
4-MeO-3-CN	25	372.2		
p-*t*-Bu	0	10.69		
	25	347.5	22.0	4.8
p-Ph	25	289.7		
β-Naph	25	230.1		
3,5-Me_2	0	1.437		
	25	53.12	22.8	2.9
4-MeS-3-CN	25	46.15		
p-F	0	1.040		
	25	38.48	22.8	2.3
m-Me	0	0.6577		
	25	25.53	23.1	2.5
H	15	3.156		
	25	12.55	22.8	0.1
	45	148.8		
m-MeO	25	6.807		
4-Me-3-Cl	25	3.638		
p-Cl	25	4.017		
p-Br	25	2.824		
m-MeS	25	1.750		
m-F	25	0.1321[c]	24.5	−3.2
	45	1.898		
	75	58.23		
m-Cl	25	0.06670[c]	25.0	−3.0
	45	1.007		
	75	32.92		
m-Br	25	0.06392[c]	24.7	−4.2
	45	0.9313		
	75	29.08		
3,4-Cl_2	25	0.06105[c]	24.2	−5.8
	45	0.8484		
	75	24.93		
m-CF_3	25	0.01124[c]	25.5	−4.7
	45	0.1795		
	75	6.308		
m-CN	25	0.004608[c]	26.1	−4.6
	45	0.07815		
	75	2.966		
p-CF_3	25	0.004408[d]		
m-NO_2	25	0.002370[d]		
p-CN	25	0.002130[d]		
p-SO_2Me	25	0.001234[d]		
3,5-Cl_2	25	0.001036[d]		

a) Calculated from linear logarithmic relation between tosylates and chlorides in 80E at 25 °C ($\log k_{OTs}=0.945 \log k_{Cl}+3.508$ ($R=0.9993$, SD=±0.032, and $n=5$)). b) Estimated based on the log k–log k relation between 0 °C and 25 °C ($\log k_{25\,°C}=0.943 \log k_{0\,°C}+1.260$ ($R=0.9998$, SD=±0.031, $n=13$)). c) Extrapolated from rate constants at other temperatures. d) Calculated from linear logarithmic relation between tosylates and *m*-nitrobenzenesulfonates at 25 °C ($\log k_{OTs}=1.090 \log k_{ONs}-1.282$ ($R=0.9999$, SD=±0.019, $n=4$)).

Table 4. Solvolysis Rates of α-*t*-Butylbenzyl *m*-Nitrobenzenesulfonates in 80% aq Ethanol

Subst.	Temp/°C	$10^5\,k/s^{-1}$	$\Delta H^{\neq}_{25°C}$	$\Delta S^{\neq}_{25°C}$
m-Me	25	729.5		
H	25	409.5		
m-Cl	25	3.273		
m-CN	25	0.2749		
p-CF_3	25	0.2670[a]	24.8	−0.9
	45	3.943		
	75	125.3		
m-NO_2	25	0.1511[a]	24.7	−2.2
	45	2.220		
	75	70.06		
p-CN	25	0.1370[a]	24.7	−2.5
	45	2.007		
	75	63.13		
p-SO_2Me	25	0.08301[a]	25.6	−0.6
	45	1.334		
	75	47.25		
3,5-Cl_2	25	0.07072[a]	25.2	−2.0
	45	1.096		
	75	37.05		

a) Extrapolated from rate constants at other temperatures.

Table 5. Solvolysis Rates of α-t-Butylbenzyl Chlorides in 80% aq Ethanol

Subst.	Temp/°C	$10^5\,k/s^{-1}$	$\Delta H^{\neq}_{25°C}$	$\Delta S^{\neq}_{25°C}$
p-MeO	0	14.29		
	25	357.8	20.3	−1.8
p-MeS	0	0.6519		
	25	20.39	21.7	−2.7
p-PhO	25	5.491		
4-MeO-3-Cl	25	2.386		
3,4-Me_2	25	0.2446[a]	22.9	−7.4
	45	2.959		
	75	72.78		
p-Me	25	0.1340[a]	21.3	−13.8
	45	1.374		
	75	27.33		
4-MeO-3-CN	25	0.05386[a]	22.8	−10.8
	45	0.6436		
	75	15.58		

a) Extrapolated from rate constants at other temperatures.

correlation of $\rho=-5.542$ and $r=1.093$ and solvolysis in 80E results in the identical LArSR correlation. The LArSR ρ value agrees with the ρ_m value within experimental uncertainty. The SD values for LArSR correlations are of the order of ±0.06 (or 0.01—0.015 σ-unit) which are just identical with the SD value for the meta correlation (of single parameter treatment). Furthermore, they are also comparable with the SD values 0.04—0.08 of log-log relations between solvents and between tosylates and nosylates (*m*-nitrobenzenesulfonates). Consequently, the precision index of ±0.015 in σ-unit may be regarded as the reference level of the acceptable conformity to the LArSR equation. Both the large negative ρ value and the enhanced r value close to (or even larger than) unity suggest that this solvolysis proceeds through a highly charged transition state of a rate-determining k_c-ionization leading to a carbocation intermediate. Furthermore, this precise linear relationship rules out either nucleophilic solvent assistance or neighboring methyl participation.

The Brown σ^+ correlations for the corresponding data set are compared in Table 6. We can clearly see that the LArSR equation can describe the present reaction more precisely than the Brown $\rho^+\sigma^+$ treatment; the SD values are twice as large as those of the corresponding LArSR correlations. The ρ^+ values are slightly more negative than the corresponding ρ_m values, and those of limited electron donors are even more negative, presumably implying the higher resonance demand of this secondary solvolysis than that of α-cumyl system, or otherwise nonlinear σ^+ correlation. Nevertheless, as a practical approximation, the σ^+ correlations in Table 6 should also be regarded as being good correlations of acceptable conformity. The simple Brown treatment provides satisfactory correlation for the present system, just within the limit of the usual accuracy of Hammett-type linear free energy relationships: The accuracy of the substituent constants is generally estimated to be ca. ±0.03 σ-unit.[14] A sophisticated treatment with an additional term should give more satisfactory results than the simpler treatment. However, essentially a small difference in the r-value between the present and Brown's reference

Table 6. Results of Correlation Analysis

Solv.	Substituent sets	Correlation	n[a]	ρ	r	SD[b]	R[c]
80A	all	LArSR	31	−5.542±0.040	1.093	0.060	0.9997
80A	all	σ^+	31	−5.852±0.051	1.00	0.114	0.9989
80A	*meta*, *p*-(+*R*)[d]	σ^0	13	−5.501±0.063		0.064	0.9992
80E	all	LArSR	30	−5.650±0.045	1.106	0.067	0.9996
80E	all	σ^+	30	−5.991±0.072	1.00	0.157	0.9980
80E	*meta*, *p*-(+*R*)[d]	σ^0	13	−5.564±0.045		0.046	0.9996

a) Number of substituents involved. b) Standard deviation. c) Correlation coefficient. d) All meta substituents and *p*-π-acceptor substituents.

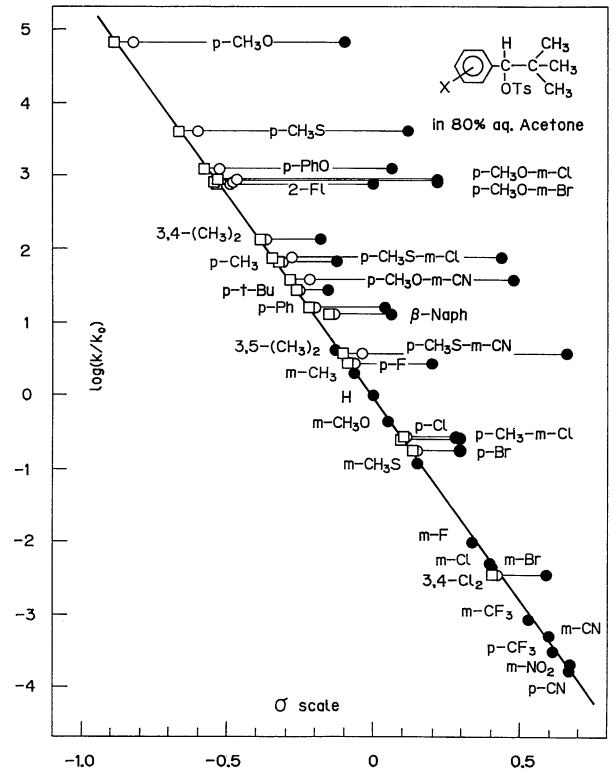

Fig. 2. LArSR plot for the solvolysis of α-t-butylbenzyl tosylates in 80A at 25°C; open circles σ^+, closed σ^0, and squares $\bar{\sigma}$ for r=1.09.

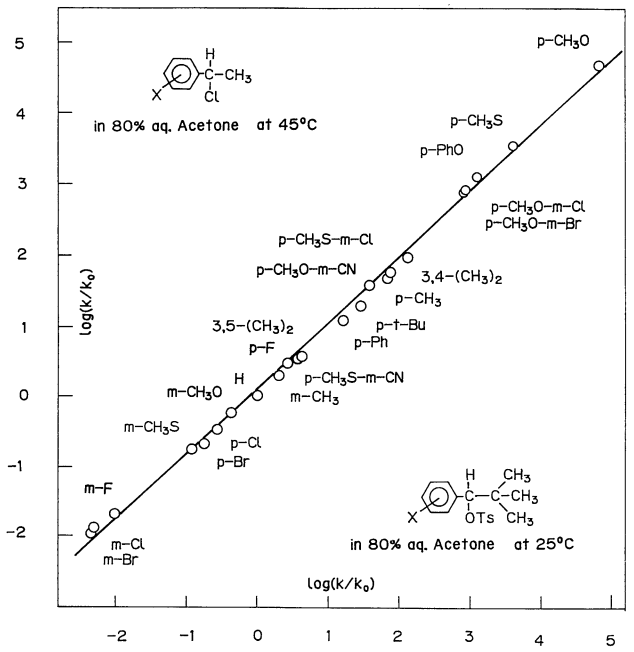

Fig. 3. log k–log k plot between solvolyses of α-t-butylbenzyl tosylates at 25°C and α-methylbenzyl chlorides at 45°C in 80A.

reactions may not result in significant improvement of the correlation with the LArSR treatment.

In the present comparison, it is not simply the overall goodness of the fit, the standard deviation or the correlation coefficient, that matters but the pattern of deviations of the plot. In Fig. 2 the σ^+ plots construct a practically good straight-line correlation, though there is a clear trend of upward curvature: More strictly speaking, strong p-π-donor substituents all deviate slightly but definitely in the direction of enhanced reactivity, to fall on a separate line parallel to the meta correlation line. The deviations are clearly proportional to the $\Delta\bar{\sigma}_R^+$ values of the substituents. This discontinuous correlation plot is indeed hardly interpreted in terms of ordinary factors other than a different resonance demand. On the other hand, the LArSR plots give a single straight line correlation for all substituents including resonance insensitive ones. The complete linearity indicates an operation of a single mechanism throughout the range of substituents.

The Resonance Demand of Secondary Benzylic Solvolysis. The present LArSR analysis provides strong evidence for the k_c ionization mechanism of this solvolysis without either nucleophilic solvent assistance or neighboring methyl participation. On the other hand, it has frequently been pointed out that most of secondary benzylic solvolyses are borderline case, as is the solvolysis of benzyl tosylates.[8-10] We have already reported on a LArSR analysis of the solvolysis of α-methylbenzyl chlorides, and pointed out that this secondary substrate has an appreciably enhanced resonance demand r value of r=1.15.[4a,b] Solvent participation may become important as the substituent becomes more electron attracting, and the σ^+ plot will be monotonically concave upwards. As a result, a reduced ρ value given by slowly solvolyzing substituents may give rise to a higher r-value in the LArSR correlation.[8,10] If this is the case, the enhanced resonance demand observed should only be an artifact of the mechanistic complexity.[8,10]

From various viewpoints, the solvolysis of α-t-butylbenzyl tosylates can be an appropriate reference scale for the analysis of substituent effects in k_c solvolyses generating secondary benzylic carbocations. The solvolysis of α-methylbenzyl chlorides in 80A shows a linear free energy relationship against the α-t-butylbenzyl solvolysis (Fig. 3) with an essentially unit slope of 0.927 (R=0.9985 and SD=±0.098). The r value for the α-t-butyl system is indetectably different from the value of 1.15 for the α-methylbenzyl system, but appears still to be detectably higher than the r value of unity for the α-cumyl system. The Brown σ^+ treatment gives the α-methylbenzyl solvolysis a bisected correlation with a ρ^+ of −5.9 for the region of the electron donor substituents and −4.95 for attracting substituents.[15] This fact led to a S_N1–S_N2 mechanistic shift with the substituent in this solvolysis. Whereas

the S_N1–S_N2 mechanistic shift may be a possible cause of the exalted r value observed in the solvolysis of α-methylbenzyl chlorides, the similarly exalted r value in the α-t-butylbenzyl system is unlikely to be attributable to the deviation from the σ^+ linearity caused by solvent participation, because of its neopentyl structure. According to Brown's assumption of the single σ^+ linearity, the substituent effect on the present system must be considered to be practically linear, both with the α-cumyl substituent effect and also with the α-methylbenzyl one. We do agree at least for these ordinary stable benzylic solvolysis systems because of insignificant differences in the r values of these three systems. This may imply, however, that the σ^+ treatment should be intrinsically incapable of detecting such a curvature of the plot of α-methylbenzyl as well as of α-t-butylbenzyl solvolysis. This close-similarity of the r value in ordinary benzylic solvolyses is indeed the source of controversies concerning the real merit of the r parameter in the Yukawa–Tsuno equation.[8,16]

For the solvolysis of α-methylbenzyl chlorides in relatively less nucleophilic aqueous TFE, where solvent participation must be unimportant, we found a linear relationship against α-t-butyl solvolysis; the r values of both systems are essentially the same as the value in 80A.[2b] The use of the Brown σ^+ may be the only reason for a curve break in the substituent effect correlation in many cases.[7b,10] The break of the linearity should be examined very carefully since it may often lead to an unlikely conclusion concerning mechanistic change.[7b,8] In conclusion, the S_N1–S_N2 mechanistic shift, even if conceivable for the α-methylbenzyl solvolysis, should be completely irrelevant to the observation of an enhanced r value in the present α-t-butylbenzyl system. The resonance demand for the secondary benzylic S_N1 solvolysis must intrinsically differ from that for α-cumyl solvolysis.

The steric loss of coplanarity of the reaction center has been pointed out as one of the important factors affecting the resonance demand r parameter. Tanida et al. reported earlier an r value of 0.491 for the solvolysis of α,α-di-t-butylbenzyl p-nitrobenzoates in 70A.[17] This remarkably reduced r value from the value of unity for most of tertiary benzylic solvolyses was attributed to the loss of coplanarity by twisting between the benzene ring and the incipient carbocation center in the transition state. The r value of the present system having one α-t-butyl group is only insignificantly reduced from the r=1.15 assigned for the α-methyl analogue and remains still exalted from the value of unity for cumyl and related stable tertiary systems. Provided the comparable polar effects of methyl and t-butyl groups, the essential identity of the r value indicates no effective twisting from coplanarity in the transition state of the α-t-butyl solvolysis.[18] The rate retardation of 10^3 by the α-t-butyl group relative to α-CH_3 should be attributed largely to destabilization due to a steric restriction of solvation in the transition state.[18]

Reexamination of the Brown σ^+. The present α-t-butylbenzyl tosylates solvolyze by a fixed k_c mechanism without any mechanistic change with substituent, and the apparent substituent effect should be characteristic of secondary benzylic solvolysis. It can consequently serve as an appropriate reference system for a critical examination of σ^+ constants.

Apparent substituent constants $\bar{\sigma}$ values in each solvent are derived using ρ value based only on meta and π-accepting para substituents, in exactly the same manner as that utilized by Brown when he defined his σ^+ values from α-cumyl solvolysis, and the results are given summarized in Table 7. The σ^+ values in the literature[4b] as well as the original Brown values[12] based on the solvolysis of substituted α-cumyl chlorides in 90A at 25 °C are also included for comparison in this Table. The apparent substituent constants, $\bar{\sigma}$ values, are consistently more negative than the corresponding Brown σ^+ values for para π-donor substituents. More strictly, the increment, $\bar{\sigma}_p-\sigma^0$, appears to be even precisely proportional to the resonance strength $\Delta\bar{\sigma}_R^+$ of substituents as shown in Fig. 4 for the aqueous acetone set. The increments $\bar{\sigma}_p-\sigma^0$ of π-donor substituents are most reasonably ascribed to the enhanced resonance contribution in this system which corresponds to the term $r\Delta\bar{\sigma}_R^+$ in the LArSR Eq. 1. Obviously, the present set of apparent

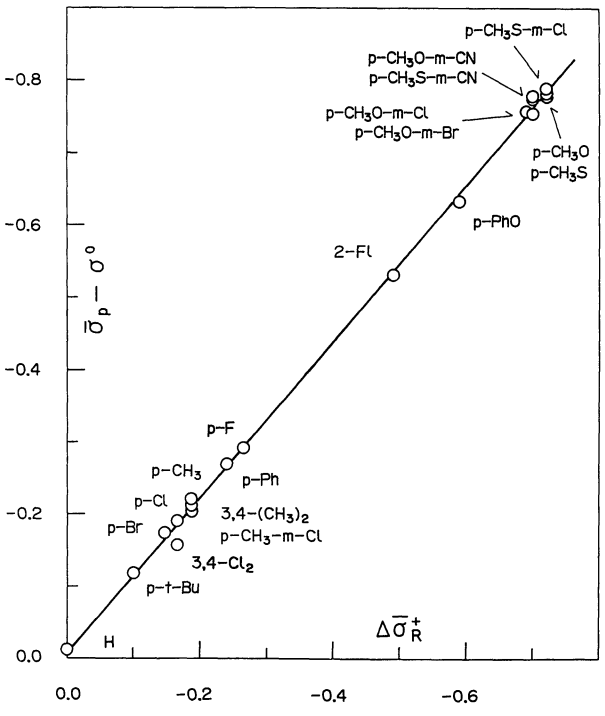

Fig. 4. The plot of resonance enhancement $\bar{\sigma}_p-\sigma^0$ for α-t-butylbenzyl solvolysis in 80A against $\Delta\bar{\sigma}_R^+$.

Table 7. Substituent Constants

Subst.	$\bar{\sigma}$(80A)[a]	$\bar{\sigma}$(80E)[a]	σ^+[b]	σ^+(80A)[c]	σ^+(80E)[d]
p-MeO	−0.882	−0.904	−0.778	−0.815	−0.828
p-MeS	−0.660	−0.696	−0.604	−0.594	−0.620
p-PhO	−0.570	−0.596	−0.539[e]	−0.515	−0.533
4-MeO-3-Br	−0.535		−0.491[f]	−0.470	
4-MeO-3-Cl	−0.539	−0.545	−0.490[f]	−0.475	−0.472
2-Fluorenyl	−0.533	−0.546	−0.491	−0.487	−0.495
3,4-Me_2	−0.394	−0.380	−0.376[g]	−0.377	−0.361
p-Me	−0.341	−0.327	−0.311	−0.324	−0.308
4-MeS-3-Cl	−0.349	−0.352	−0.270[f]	−0.282	−0.276
4-MeO-3-CN	−0.296	−0.263	−0.255[f]	−0.231	−0.189
p-*t*-Bu	−0.272	−0.258	−0.256	−0.262	−0.247
p-Ph	−0.228	−0.244	−0.179	−0.205	−0.218
β-Naph	−0.213	−0.226	−0.135	−0.195	−0.205
3,5-Me_2	−0.125	−0.113	−0.128[g]	−0.125	−0.113
4-MeS-3-CN	−0.115	−0.102	−0.043[f]	−0.050	−0.028
p-F	−0.089	−0.088	−0.073	−0.065	−0.061
m-Me	−0.067	−0.057	−0.066	−0.067	−0.057
H	−0.012	−0.002	0.000	−0.012	−0.002
m-MeO	0.055	0.045	0.047	0.055	0.045
4-Me-3-Cl	0.094	0.093	0.110[g]	0.111	0.113
p-Cl	0.092	0.085	0.114	0.108	0.103
p-Br	0.124	0.112	0.150	0.138	0.128
m-MeS	0.156	0.149	0.158	0.156	0.149
m-F	0.352	0.348	0.352	0.352	0.348
m-Cl	0.406	0.400	0.399	0.406	0.400
m-Br	0.409	0.404	0.405	0.409	0.404
3,4-Cl_2	0.434	0.407	0.424[f]	0.449	0.425
m-CF_3	0.544	0.537	0.520	0.544	0.537
m-CN	0.583	0.606	0.562	0.583	0.606
p-CF_3	0.623	0.609	0.612	0.623	0.609
m-NO_2	0.653	0.657	0.674	0.653	0.657
p-CN	0.669	0.665	0.659	0.669	0.665
p-SO_2Me	0.688	0.707	0.697[h]	0.688	0.707
3,5-Cl_2	0.739	0.721	0.701[i]	0.739	0.721

a) Apparent $\bar{\sigma}$ values of α-*t*-butylbenzyl tosylates: $\bar{\sigma}=(\log k/k_0)/(-5.542)$ for 80A and $\bar{\sigma}=(\log k/k_0)/(-5.650)$ for 80E. b) Calculated from solvolysis of α-cumyl chlorides in 90A at 25 °C; Ref. 12. c) σ^+ values calculated from $(\bar{\sigma}(80A)-0.093\Delta\bar{\sigma}_R^+)$. d) σ^+ values calculated from $(\bar{\sigma}(80E)-0.106\Delta\bar{\sigma}_R^+)$. e) Ref. 4a. f) Ref. 4b. g) Ref. 12d. h) X. Creary, M. E. Mehrsheikh-Mohammadi, and M. D. Eggers, *J. Am. Chem. Soc.*, **109**, 2435 (1987); in EtOH. i) X. Creary, *J. Am. Chem. Soc.*, **103**, 2463 (1981); in EtOH.

substituent constants should be referred to as the substituent constants of r=1.093 in the resonance demand scale.

A set of secondary σ^+ values in the Brown scale, i.e., the values at r=1.00 in our resonance demand (r) scale, are derived from the apparent $\bar{\sigma}$ values for *p*-π-donors in 80A and 80E by the calibration for the resonance enhancements. Because of the absolutely small calibration term $(r-1.00)\Delta\bar{\sigma}_R^+$ for the r value, the uncertainty involved in the $\Delta\bar{\sigma}_R^+$ parameters employed will not affect the calculated σ^+ values. The calculated values are compared with the σ^+ values available in the literature. The Brown σ^+ values can be accurately reproduced in this manner within ±0.01 in σ^+ unit. Both the σ^+ sets in aq ethanol and in aq acetone are in precise agreement within ±0.01 in σ unit for all typical substituents except *p*-MeO, *p*-MeS, *p*-PhO, 4-MeO-3-CN, and 4-MeS-3-CN groups. It is worthy of note that the σ^+ value of *p*-MeO is appreciably more negative than Brown's value, and that the σ^+ value derived from the present system is identical to a value of −0.82 estimated from α-methylbenzyl[4a] or from benzhydryl solvolysis.[19] Thus, the Brown σ^+ value for the *p*-MeO group must involve a relatively large uncertainty caused by remote extrapolation for its extremely high reactivity in the cumyl chloride solvolysis.[12a] We already pointed out an exalted σ^+ value for the *p*-MeO group in a correlation analysis of substituent effects on the relevant σ^+-type solvolysis reactivities in aqueous acetone solution.[4a] A revised σ^+ value of −0.54[12c] for *p*-MeS group was recently proposed by Brown et al., whereas the present result lends support for the preference of the original σ^+ value of −0.60 for this group.[12a] It should be emphasized that the poor constancy of the σ^+ values of strong *p*-π-donor substituents appears to arise in most cases from changes in the resonance demand with the system, rather than from mechanistic complexity. We should take into

account the effect of varying resonance demand before analyzing the solvent-dependence of the σ^+ value.

Deviations of a few particular substituents from the simple linearity in Fig. 1 may be attributed to the solvent modification of their substituent effects caused by a specific solvent-substituent interaction, but practically the solvent changes of substituent constant values are not very serious in these solvents. Thus, the set of σ^+ values listed in Table 7 can be applied to the substituent effect analysis of the reactivity data in aq. acetone and in aq. EtOH. However, a set of precise $\bar{\sigma}$ values in each solvent accounting for the solvent-modification will be needed for precise substituent effect analysis. The present α-*t*-butylbenzyl system is useful for determining solvent-modified σ^+ constants.

The apparent $\bar{\sigma}$ constants for electron attracting meta substituents are close to the σ_m^+ rather than to σ_m^0 values, even though σ^0 and σ^+ values for these deactivating groups may be generally assumed to be identical. This appears to be rather general[5] while more relevant data must be required. Most of electron-attracting substituents in the solvolysis of α-methylbenzyl chlorides in 50A in fact show an excellent linear relation against the α-*t*-butylbenzyl substituent effect in 80A (R=0.9995, SD=±0.063, n=18) as in Fig. 5. While the α-methylbenzyl solvolysis has often been suggested to be subject to solvent nucleophilic assistance,[9] the above linear correlation provides strong support for the absence of solvent nucleophilic assistance in the solvolysis of strongly electron attracting substituents in 50A solvent.

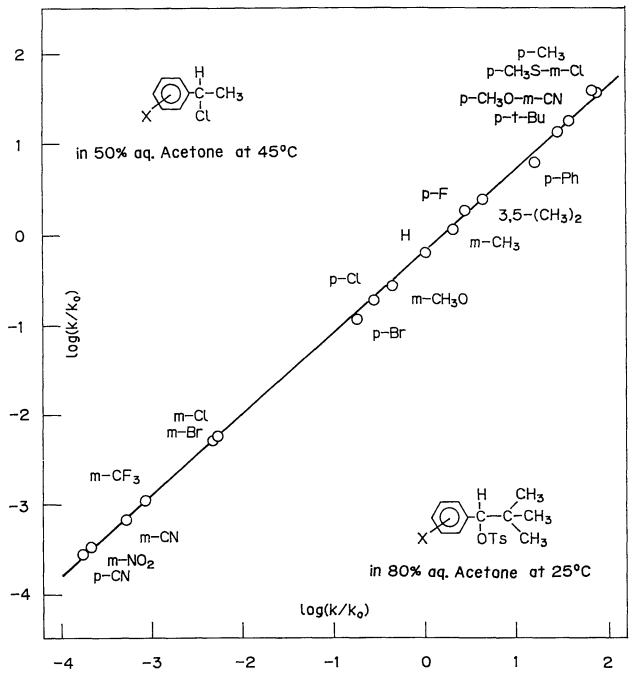

Fig. 5. Linear logarithmic rate relationship between solvolyses of α-*t*-butylbenzyl tosylates (80A, 25 °C) and α-methylbenzyl chlorides (50A, 45 °C).

The σ^+ values of *m*-CN and *m*-NO_2 are found to be slightly less electron attracting than their σ^0 or σ values, whereas the values of *m*- and *p*-CF_3 groups are slightly more attracting than their σ^0 values. These deviation behaviors are commonly observed in most benzylic solvolyses,[20] but the reasoning will not be immediately possible. In particular, the more enhanced electron withdrawal by the CF_3 group at either meta or para position in the more electron deficient system does not appear to be theoretically explicable in terms of ordinary electronic effects. We must wait for more sufficient data to substantiate the unususl behavior of this substituent.

Experimental

Materials. Substituted phenyl *t*-butyl ketones (pivalophenones): Most of substituted phenyl *t*-butyl ketones were synthesized according to Ford's procedure.[21] Grignard reagant prepared from an appropriately substituted bromobenzene and magnesium in ether was added dropwise to the ethereal solution of 10% excess of pivaloyl chloride at −15 °C. After stirring overnight the reaction mixture was decomposed with an 18% HCl solution, extracted with ether, washed with 10% NaOH, and dried over $MgSO_4$. Crude ketones obtained were purified by silica-gel column chromatography or by distillation.

4-MeO-3-Br and 4-Mes-3-Br pivalophenones were obtained by bromination of *p*-MeO and *p*-MeS pivalophenones. Bromine (2 equiv) was added to ketone in acetic acid at 50 °C with stirring. The reaction mixture was poured into water, treated with $NaHSO_3$, extracted with ether, and purified by silica-gel column chromatography.

4-MeO-3-CN, 4-MeS-3-CN, *p*-CN, and *m*-CN derivatives were prepared from the bromo precursors by the Friedman–Shechter method.[22] The bromo derivatives were refluxed with copper(I) cyanide (2 equiv) in DMF for 6 h. The reaction mixture was decomposed with $FeCl_3$–hydrochloric acid, extracted with benzene, and purified by silica-gel column chromatography.

m-Nitropivalophenone was prepared by nitration of the unsubstituted ketone, according to the typical procedure for the nitration of acetophenone.[23] To the ketone dissolved in concd sulfuric acid, a mixture of concd nitric acid and concd sulfuric acid was added at −15 °C. The reaction mixture was poured into ice water, extracted with ether and purified by silica-gel column chromatography (oil).

p-$MeSO_2$ pivalophenone was prepared by the oxidation of *p*-MeS derivative, by refluxing for 4 h in 35% H_2O_2–acetic acid and purified by silica-gel column chromatography, mp 77.0—87.0 °C.

Substituted α-*t*-butylbenzyl alcohols: All the substituted alcohols were prepared from corresponding ketones by reduction with $NaBH_4$ in ethanol at room temperature. The obtained alcohols were purified by silica-gel column chromatography.

Substituted α-*t*-butylbenzyl arenesulfonates: Most of the arenesulfonates were synthesized according to a modified Liu's method.[10] Commercial butyllithium in hexane, 1.62 mol dm^{-3} (1 equiv), was added dropwise to α-*t*-

butylbenzyl alcohol in THF at 0 °C with stirring under a nitrogen atmosphere. The mixture was stirred for 1 h; then, *p*-toluenesulfonyl chloride or *m*-nitrobenzenesulfonyl chloride (1 equiv) in THF was added dropwise at −40 °C. After stirring overnight, the reaction mixture was poured into ether, washed with cold water and dried over $MgSO_4$. In the case of highly unstable *p*-MeO and *p*-MeS derivatives, the solvent ether was removed under vacuum to dryness to give solid ester without treatment with cold water to avoid hydrolysis. The esters were purified by repeated recrystallization from benzene–hexane.

α-*t*-Butyl-(*m*-nitro)benzyl *m*-nitrobenzenesulfonate was prepared by the Tipson procedure[24] from the corresponding alcohol and *m*-nitrobenzenesulfonyl chloride in pyridine.

Physical and analytical data of arenesulfonates are summarized in Table 8.

Solvents. Commercial acetone was refluxed with $KMnO_4$ for 6 h and distilled. The distillate was dried over anhydrous Na_2CO_3 for two days and fractionated. Ethanol (95%) was dehydrated twice by refluxing with magnesium ethoxide. Deionized water was refluxed with $KMnO_4$ and distilled, and redistilled immediately before use.

Aqueous organic solvents (80% acetone and 80% ethanol) were prepared by mixing corresponding volumes of two components at 25 °C.

Kinetic measurement. The solvolysis rates in aqueous organic solvents were followed in the usual manner according to a conductometric method described before.[25]

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 relatively fast reacting substrates, a complete solution can be attained relatively quickly by adding a substrate dissolved in a small amount of organic component of the solvent into the thermostated solvent in a cell flask involving adjustable amount of water.

The rates of solvolysis for slow reacting substrates at high temperatures were followed by using the ampoule technique with a conductivity determination. The reaction was quenched by rapid cooling with ice-water at appropriate intervals over 2 half-lives. The quenched ampoule was opened and fitted with a conductivity cell and the

Table 8. Physical Data of α-*t*-Butylbenzyl Arenesulfonates

Subst.	Mp/°C	Carbon/%		Hydrogen/%		Nitrogen/%	
		Found	Calcd	Found	Calcd	Found	Calcd
Tosylates							
p-PhO[a]	50.0—51.0						
4-MeO-3-Cl[a]	68.5—69.0						
3,4-Me_2	49.5—50.5	69.29	69.33	7.58	7.56		
4-MeS-3-Cl	67.8—68.2	57.04	57.20	5.72	5.81		
p-Me	52.0—53.0	68.65	68.64	7.24	7.28		
4-MeO-3-CN	85.0—88.0	64.27	64.32	6.12	6.21	3.63	3.75
p-*t*-Bu	56.0—57.0	70.52	70.55	8.03	8.07		
p-Ph	66.2—66.5	73.06	73.06	6.65	6.64		
β-Naph[a]	58.0—58.5						
3,5-Me_2	67.5—68.0	69.32	69.33	7.60	7.56		
4-MeS-3-CN	94.5—98.1	61.54	61.67	6.03	5.95	3.62	3.60
p-F	65.8—66.9	64.32	64.26	6.41	6.29		
m-Me	64.0—65.0	68.64	68.64	7.26	7.28		
H	68.2—68.9[b]	67.95	67.89	6.98	6.96		
m-MeO	66.5—67.5	65.41	65.49	6.83	6.94		
4-Me-3-Cl	74.0—78.0	62.17	62.20	6.27	6.32		
p-Cl	67.8—68.0	61.18	61.27	5.95	6.00		
p-Br	64.5—64.7	54.82	54.41	5.46	5.33		
m-MeS	71.0—72.8	62.55	62.60	6.74	6.64		
m-F	71.8—72.2	64.32	64.26	6.29	6.29		
m-Cl	83.0—84.0	61.34	61.27	6.03	6.00		
m-Br	73.5—75.0	54.59	54.41	5.29	5.33		
3,4-Cl_2	94.0—95.0	55.90	55.82	5.21	5.20		
m-CF_3	77.6—78.1	59.06	59.05	5.49	5.48		
m-CN	77.0—77.5	66.67	66.45	6.23	6.16	3.86	4.08
m-Nitrobenzenesulfonates							
m-Me	51.8—52.0	59.64	59.49	5.76	5.82	3.73	3.85
H	53.0—54.0	58.41	58.44	5.61	5.48	3.95	4.01
m-Cl	69.5—70.0	53.38	53.19	4.82	4.73	3.63	3.65
m-CN	102.0—103.0	58.02	57.74	4.93	4.85	7.23	7.48
p-CF_3	73.0—74.0	51.90	51.80	4.40	4.35	3.35	3.36
p-CN	98.0—99.0	57.72	57.74	4.76	4.85	7.41	7.48
m-NO_2	82.3—82.7	52.09	51.77	4.68	4.60	7.09	7.10
p-SO_2Me	102.5—103.0	50.52	50.57	4.86	4.95	3.25	3.28
3,5-Cl_2	86.9—87.3	48.99	48.81	4.18	4.10	3.40	3.35

a) Unstable to give accurate elemental analysis. b) Lit,[11] mp 75—76 °C.

conductivity readings were taken after equilibration at a sufficiently low temperature. Several ampoules were allowed to react for 10 half-lives at higher temperature to provide an infinity reading.

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

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