© 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 1146—1153 (1990) [Vol. 63, No. 4

Substituent Effects. XXI.[1] Solvolysis of Benzyl Tosylates

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(Received October 11, 1989)

The rates of solvolyses of a series of substituted benzyl tosylates were determined in 80% aqueous acetone, and the substituent effect was analyzed based on the Yukawa-Tsuno LArSR Eq. The LArSR Eq. as well as Hammett-Brown treatment failed to give any simple linear plot for the effect of the full range of substituents, indicating a significant mechanistic shift. The σ^+ plot gave a split pattern of parallel curvatures with significant gaps for strong π-donors, weak π-donors, and non-conjugative substituents, respectively. The widely split σ^+ plot conflicts with the accepted interpretation in terms of the k_c—k_s mechanistic transition, since the k_c—k_s mechanistic change should result in a single smooth-curved plot, only if plotted against an appropriate substituent constant scale. The plots of para π-donors against an appropriate $\bar{\sigma}$ scale with r=1.3 coalesced into a single smooth curve including the meta correlation curve. A sufficiently linear LArSR plot with r=1.3 for the reactive substituents down to 4-MeS-3-CN group can be referred to the substituent effect correlation for the k_c mechanism of this system. The result of a correlation analysis confirmed this conclusion, giving a best ρ value of −5.23 and an r value of 1.28 for a range of substituents more activating than 4-MeS-3-CN. The r value for the k_c solvolysis of activated range of substituents was found to be identical with the r value obtained for the gas-phase stability of benzyl cation. The enhanced resonance demand (r=1.28) obtained in the benzyl solvolysis must be an intrinsic feature characterizing the nature of the transition state of k_c solvolysis of benzyl tosylate, rather than a correlational artifact of the nonlinearity caused from mechanistic complexity.

The Yukawa and Tsuno LArSR equation[2] has been applied to a series of solvolyses, providing important information for estimating the nature of transition states,[1,3–10]

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

The resonance demand r value has been found to change widely with the reaction, not only within a range lower than unity, as defined for the α-cumyl (1-methyl-1-phenylethyl) system ($0<r<1$), but to also be significantly higher than unity ($r<1$) in many cases. This fact clearly indicates that the Brown σ^+ value (r=1.0) does not reflect the highest extreme of benzylic resonance exaltation but, rather, is merely a point in the r scale of resonance exaltation effect. This r scale permits an evaluation of the nature of the transition state, and has been widely applied to the assignment and interpretation of reaction mechanisms.[1,3–10] Substituent effects on those systems having an extremely high or low r value, r=0.57 for solvolysis of neophyl brosylates (2-methyl-2-phenylpropyl *p*-bromobenzenesulfonates)[4,7] and 1.40 for 1-CF_3-1-phenylethyl tosylates,[6–8] are far beyond the scope of the simple Brown σ^+ treatment.

$$\log(k/k_0) = \rho^+\sigma^+ \tag{2}$$

However, question has also been raised regarding the real merit of the r parameter, as well as the validity of Eq. 1.[10–12] It is suggested that the deviation of the r value from unity should in most cases be an artifact of mechanistic complexity. A well-known example of the target of controversy[10] is the substituent effect on the solvolysis of benzyl tosylates.[13–17] Brown et al. demonstrated earlier a bisected (bilinear) correlation with their σ^+ giving different ρ^+ values for the regions of activating and deactivating substituents, and gave a reasonable interpretation for the break in terms of a mechanistic change from the k_c mechanism for activating substituents to the k_s mechanism for deactivating ones.[14a] While the Brown σ^+ scale was utilized as a reference in all of the previous studies for the substituent effect in this system,[13c,14–16] it also appears likely that this solvolysis may have a different r value from unity, defined for α-cumyl solvolysis. For this situation, Shorter notes that the pronounced deviation from conformity to σ^+ in a direction to $r \gg 1.0$ in benzyl solvolysis is considered to be due to changing proportions of the k_c and the k_s mechanisms, and that the r value, if calculated, would not give information on the resonance stabilization of the incipient benzyl cation, compared with the α-cumyl cation.[10] For a system in which a mechanistic transition is evident, as in the present system, there is no reason to assume a single linear substituent effect relationship for the whole range of substituents. The arguments so far are based upon a simple fact that the curved plot is not straightened, even by the application of the Brown σ^+ constant. There has been no direct evidence indicating that the σ^+ scale, as defined explicitly by r=1.00 in Eq. 1, most reasonably describes the substituent effect on the k_c process of this system. The purpose of our study was to clarify whether the resonance demand in the k_c solvolysis of benzyl tosylates differs from the demand in the α-cumyl solvolysis. Since nucleophilic solvent participation may be important in this reaction, an analysis of substituent effects on the k_c reaction of this solvolysis should be applied to the severely limited range of sufficiently activating substituents and any estimation of the r value must be absolutely free from the nonlinearity caused by a mechanistic shift. The previous arguments were only for the behavior of a few typical substituents.[13–16] More substituent effect data for strong para π-donors are needed in order to discuss precisely the resonance demand characteristic of the k_c solvolysis of benzyl tosylates. We have determined the rate data of some important substituents, and the effects have been analyzed based on our LArSR Eq. 1 in comparison with the Brown σ^+ treatment.

Results

The rates of solvolyses of a series of benzyl tosylates were determined in 80 vol% aqueous acetone (80A). The solvolysis data are summarized in Table 1. The rates of strongly activating *p*-MeO and *p*-MeS derivatives were too fast to be followed in an 80A solution by the ordinary conductometric method. Accordingly, the rates of these derivatives were determined in slower solvolyzing, 96.2% aqueous acetone (96A) or by solvolysis of the corresponding chlorides. The rate of the *p*-methylthio derivative in 80A was extrapolated from the rate in 96A based on the linear free energy relationship over the range from *p*-Me to *p*-PhO between solvolysis rates in 80A and 96A at 25 °C; $\log k_{80A}=1.031 \log k_{96A}+1.978$. The rate of the *p*-MeO derivative was estimated from the solvolysis data of the chloride based on the ratio of tosylate-chloride reactivities of *p*-MeS and *p*-PhO derivatives.

The substituent effect of the benzyl solvolysis in 80A is shown by the so-called LArSR plot in Fig. 1. The plots of *m*-substituents and *p*-π-acceptor ones fall on a single smooth curve. Since their effects are essentially insensitive to the *r* value of the reaction, these substituents unequivocally define the nonlinear ρ correlation line in terms of a definite σ scale. Thus, this ρ_m curve represents the substituent effect correlation reflecting the actual k_c—k_s mechanistic shift with substituents, and may be a rigid reference of correlation analysis. The plot against σ^+ is neither simply linear nor bilinear but, rather, displays a split pattern of apparently parallel curvatures with significant gaps for strong π-donors, for weak π-donors such as alkyl groups, and for non-conjugative *m*-substituents including *p*-π-acceptors. No simple linear relation against any set of substituent constants can be

Table 1. Solvolysis of Benzyl Tosylates in 80% Aq Acetone[a)]

Subst.	Temp/°C	10^5k/s^{-1}	$\Delta H^{\ddagger}_{25\,°C}$ kcal mol^{-1} [b)]	$\Delta S^{\ddagger}_{25\,°C}$ e.u.[b)]	Subst.	Temp/°C	10^5k/s^{-1}	$\Delta H^{\ddagger}_{25\,°C}$ kcal mol^{-1} [b)]	$\Delta S^{\ddagger}_{25\,°C}$ e.u.[b)]
p-MeO	25.0	83000[c)]			*m*-MeO	25.0	1.08	19.1	−17.3
p-MeS	25.0	6970[d)]				45.0	8.70		
p-PhO	25.0	1830			*p*-Cl	25.0	0.963	18.8	−18.6
4-MeO-3-Cl	25.0	1134				35.0	2.714		
2-Fluorenyl	25.0	755				45.0	7.589		
3,4,5-Me_3	25.0	149.9			*p*-Br	25.0	0.8167		
4-MeS-3-Br	0.0	6.08			*m*-F	25.0	0.272		
	25.0	130.2	19.2	−7.2	*m*-Cl	25.0	0.256	18.7	−21.5
4-MeS-3-Cl	25.0	117.5				45.0	1.975		
3,4-Me_2	25.0	60.8			*m*-Br	25.0	0.253	18.8	−21.0
4-MeO-3-CN	25.0	47.9				45.0	1.985		
p-Me	0.0	1.30			*m*-CF_3	25.0	0.173[f)]		
	25.0	29.1	19.5	−9.2		45.0	1.360		
p-Et	25.0	22.2			*m*-CN	25.0	0.166[f)]		
p-*i*-Pr	25.0	17.68				45.0	1.310		
p-*t*-Bu	25.0	13.0			*p*-CN	25.0	0.130[f)]		
p-Ph	25.0	9.65				45.0	1.019		
2-Naph	25.0	6.54			*p*-CF_3	25.0	0.146[f)]		
4-MeS-3-CN	25.0	6.32				45.0	1.146		
3,5-Me_2	25.0	3.709	19.5	−13.6	*p*-NO_2	25.0	0.0997[g)]	18.6	−23.5
	45.0	31.1				35.0	0.285[e)]		
p-F	25.0	3.013	19.3	−14.6		45.0	0.7694		
	45.0	24.75				55.0	1.93[e)]		
m-Me	25.0	2.262	19.0	−16.0	3,5-$(CF_3)_2$	25.0	0.0601[g)]	18.9	−23.5
	45.0	18.12				45.0	0.4772		
H	25.0	1.41	18.8	−17.6		75.0	6.833		
	45.0	11.80							

a) By volume at 25 °C. Conductometric method. b) 1 cal=4.184 J and 1 e.u.=4.184 J K^{-1} mol^{-1}. c) Calculated from rate data for benzyl chlorides in 80A at 45 °C based on chloride-tosylate logarithmic rate relation (chlorides in 80A at 45 °C, *p*-MeO, 5.321×10^{-4}s^{-1}; *p*-MeS 3.048×10^{-5}s^{-1}; *p*-PhO, 6.509×10^{-6}s^{-1}). d) Calculated from rate data in 96.2% aq acetone (50 ml acetone+2 ml H_2O) by logarithmic rate plots between 80 A and 96.2 A at 25 °C (tosylates in 96.2A at 25 °C, *p*-MeS, 9.11×10^{-4}s^{-1}; *p*-PhO, 2.74×10^{-4}s^{-1}; 2-fluorenyl, 9.64×10^{-5}s^{-1}. 3,4,5-Me_3, 2.20×10^{-5}s^{-1}; 4-MeS-3-Cl, 1.58×10^{-5}s^{-1}; 3,4-Me_2, 9.05×10^{-6}s^{-1}; *p*-Me, 4.96×10^{-6}s^{-1}). e) Titrimetrically determined. f) Calculated from the rate at 45 °C by logarithmic rate plot between 25 °C and 45 °C. g) Calculated from rate data at other temperatures.

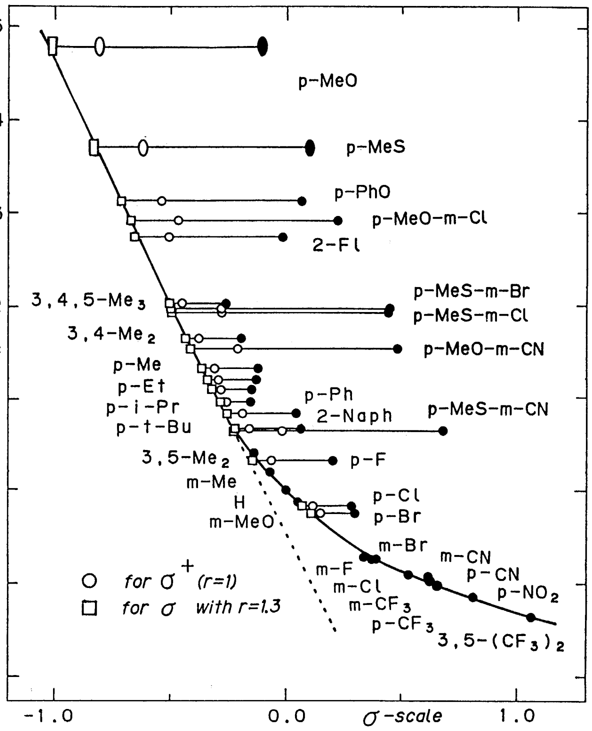

Fig. 1. The LArSR plot of solvolysis of benzyl tosylates; open circles σ^+, closed σ^0, and squares $\bar{\sigma}$ for r=1.3.

observed for a full range of substituents. The widely split figure of the σ^+ correlation is not quite consistent with the well-known simple bisected figure cited in most textbooks.[13–16]

The LArSR plots of para π-donors given by open squares against an appropriate $\bar{\sigma}$ scale coalesced into a common single curve with meta and π-acceptor para substituents. The reactive portion of substituents, down to the 4-MeS-3-CN group, shows a sufficiently linear plot over a 10^4 range of reactivity against the LArSR substituent constants $\bar{\sigma}$ with r=1.3.

The LArSR Eq. 1 has been applied statistically to varying ranges of substituents by the ordinary least-squares method, and the results of the LArSR analysis are summarized in Table 2.

From a general survey of the LArSR correlations we have confirmed that the equation is generally accurate to ca. an average precision of ±0.015 in SD/ρ scale for most substituents in the typical k_c solvolysis reactions of uncomplicated mechanisms.[9] This can serve as a practical criterion, a reference limit to assess the acceptable conformity of the present reaction to Eq. 1. Thus, the LArSR correlation for the present reaction having a ρ value of ca. −5 is expected to be accurate to the order of ±0.08—±0.10 in the SD for log k.

The LArSR correlation calculated for set No. 1 for

Table 2. Results of Correlation Analysis of Solvolysis of Benzyl Tosylates in 80% Aq Acetone

No.	Substituent set	Correlation	n[a]	ρ	r	SD[b]	R[c]
1	All	LArSR	33	−2.336	1.830	0.462	0.9567
		σ^+	33	−3.159		0.613	0.9198
2	delet.<*m*-CF_3[d]	LArSR	27	−3.583	1.391	0.337	0.9731
		σ^+	27	−4.431		0.456	0.9481
3	delet.<*m*-Hal.[d]	LArSR	24	−4.462	1.288	0.204	0.9888
		σ^+	24	−5.319		0.365	0.9620
4	delet.<*p*-Hal.[d]	LArSR	21	−4.947	1.256	0.135	0.9947
		σ^+	21	−5.817		0.346	0.9626
5	delet.<H[d]	LArSR	20	−5.057	1.261	0.104	0.9967
		σ^+	20	−5.875		0.353	0.9593
6	delet.<*m*-Me[d]	LArSR	18	−5.180	1.268	0.072	0.9983
		σ^+	18	−5.913		0.373	0.9516
7	delet.<3,5-Me_2[d]	LArSR	17	−5.231	1.279	0.040	0.9995
		σ^+	17	−5.830		0.381	0.9478
8	No.1 without disubst.[e]	LArSR	28	−1.768	3.103	0.333	0.9790
		σ^+	28	−3.058		0.641	0.9165
9	No.2 without disubst.[e]	LArSR	22	−2.802	1.984	0.276	0.9843
		σ^+	22	−4.332		0.477	0.9495
10	No.3 without disubst.[e]	LArSR	19	−3.808	1.557	0.177	0.9929
		σ^+	19	−5.312		0.349	0.9705
11	No.4 without disubst.[e]	LArSR	16	−4.515	1.371	0.145	0.9951
		σ^+	16	−6.065		0.258	0.9833
12	No.5 without disubst.[e]	LArSR	15	−4.723	1.345	0.113	0.9970
		σ^+	15	−6.255		0.244	0.9847
13	No.6 without disubst.[e]	LArSR	13	−4.903	1.329	0.082	0.9984
		σ^+	13	−6.652		0.211	0.9882
14	No.7 without disubst.[e]	LArSR	12	−4.965	1.339	0.037	0.9997
		σ^+	12	−6.744		0.216	0.9874

a) Numbers of substituents involved. b) Standard deviations. c) Correlation coefficient. d) Deleted the substituent and the less reactive ones. e) Deleted 4-MeO-3-Cl, 4-MeO-3-CN, 4-MeS-3-Br, 4-MeS-3-Cl, and 4-MeS-3-CN.

all substituents is obviously unsatisfactory in reference to this acceptance level. The exclusion of more deactivating substituents than *m*-Me (No. 6) improves the precision of the fit to satisfy the criterion (an SD of ±0.07) of acceptable conformity. The precision of the fit is improved to arrive at a minimum SD value of ca. ±0.04 for a limited substituent range down to the 4-MeS-3-CN group (set No. 7). The best-fit ρ and r values do not change any more by further restricting the substituent range. Only for such a severely restricted range of activating substituents, can an acceptable LArSR correlation be obtained with an r value of 1.3. The corresponding Brown $\sigma^+\rho^+$ correlations for these sets (in Table 2) are all distinctly poor in reference to the above acceptable conformity level. In fact, a slightly better $\sigma^+\rho^+$ correlation can be obtained by deleting more deactivating groups than *m*-halogens (set No. 3), whereas an SD value of >0.3 is not improved any more by further limiting the range of substituents.

Discussion

In the solvolysis of substituted benzyl tosylates, the k_c mechanism will be predominant for activating substituents, and the k_s mechanism will be more important for strongly deactivating substituents. Substrates reacting by the k_c mechanism should satisfy a linear substituent effect relationship with an appropriate substituent constant scale. Likewise, the deactivated range of substrates reacting by the k_s mechanism will satisfy a linear relation for the k_s mechanism. The k_c-k_s mechanistic shift should be also a continuous function of the substituent polarities, and should result in a single smooth-curved or a bisected correlation for the whole range of substituents when plotted against an appropriate set of substituent constants. Consequently, the significant split figure of the σ^+ plot in Fig. 1 clearly conflicts with the accepted interpretation in terms of the k_c-k_s mechanistic change, and points to the inadequacy of the Brown σ^+ scale for describing the substituent effects of this reaction.

The key principle of our analysis is, therefore, simply that only with an appropriate scale of the substituent constants, $\bar{\sigma}$, described by Eq. 1, will the split plot coalesce into a single concave line including deactivated k_s substrates. A simple inspection reveals that a unique resonance demand as high as r=1.3 is required in order to give a smooth single-curve correlation for the entire substituent range without any splitting. The overall correlation for whole substituents is, of course, poor and, undoubtedly, the poor fit may indicate an involvement of substrates reacting by the k_s mechanism in the set. The exclusion of more deactivating substituents than *m*-Me (set No. 6 in Table 2) is required for the precision of the fit to achieve the acceptable conformity. By a further exclusion of substituent points, the precision of the fit is a little more improved to give an optimum SD value of ca. ±0.04 (set No. 7). The best-fit ρ and r values do not change any more by further restricting the substituent range, and the consideration of minor changes in the SD value below the acceptance level does not appear to be very fruitful.

The acceptable LArSR correlation can be obtained only for a severely restricted range of activating substituents, and this r value of 1.3 must refer to the substituent effect correlation for the k_c mechanism of this system. The present estimation of the r value for the k_c mechanism excludes any effect of deactivated derivatives where the k_s mechanism would be concurred, and allows one to define the boundary of substrates reacting by the k_c mechanism.

The corresponding Brown σ^+ correlations for these sets in Table 2 are all distinctly poor in reference to the above acceptable conformity level. While the σ^+ correlations are also improved slightly by deleting the substituents more deactivating than *m*-halogens (set No. 3), the precision of the fit of ±0.3 in SD is no more improved by further limiting the range of substituents. It is apparent that the σ^+ analysis is incapable of diagnosing the mechanistic change evidently occurring in the *p*-halogen derivatives. The interpretation in terms of the k_c-k_s mechanistic transition given so far can not be applied to the scattered σ^+ correlation of this reaction. The basic requirement for this interpretation is an adequate substituent effect scale (i.e., a scale with a resonance demand r=1.3) to give a single continuous plot without split.

A reduced ρ value of -0.95 for the electron-withdrawing range suggests a reduced central charge development in the transition state in the solvent-assisted mechanism. A nonlinear σ^+ plot has recently been pointed out for solvolysis in 97%HFIP.16) The break may be attributed to a mechanistic change due to nucleophilic solvent participation, even in a relatively nonnucleophilic HFIP solvent. It should be recalled that the ρ^+ value for the k_s portion in HFIP16) is comparable with the LArSR ρ value assigned for the k_c mechanism in relatively nucleophilic solvents.

The mechanistic involvement of solvent nucleophilicity should always be a source of contradiction in the interpretation of solvolytic behavior.10,12) It is, therefore, highly instructive to compare the substituent effects on solvolytic processes with those on the corresponding carbocation stabilities in the gas phase. Recently, we have reported on the substituent effect on the gas phase chloride-transfer equilibrium of benzyl chlorides,18) which can be directly referred to the relative stabilities of substituted benzyl cations in the gas phase. The gas-phase equilibrium,

$$C_6H_5CH_2Cl + XC_6H_4CH_2^+ \rightleftharpoons C_6H_5CH_2^+ + XC_6H_4CH_2Cl,$$

is intrinsically free from mechanistic involvement of the solvent as a nucleophile and provides direct infor-

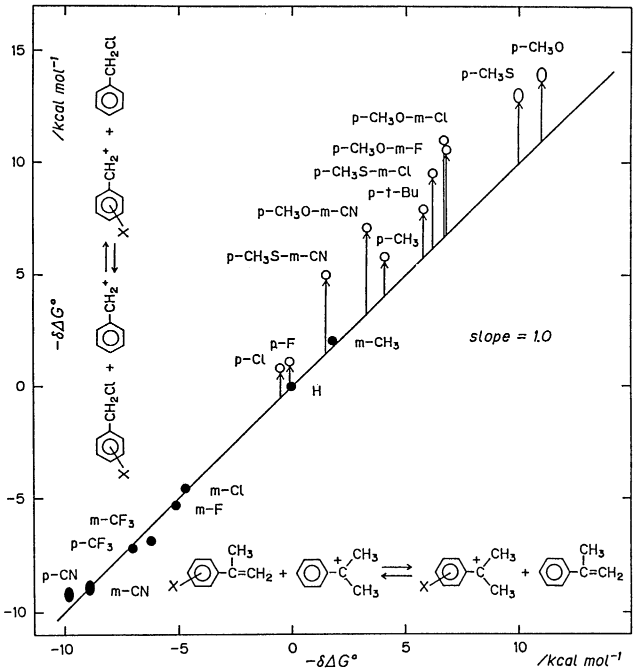

Fig. 2. Plot of chloride affinities of substituted benzyl cations against stabilities of α-cumyl cations in gas phase.

mation on the k_c ionization process of this solvolysis. The relative chloride affinities of substituted benzyl cations are plotted in Fig. 2 against the corresponding gas-phase stabilities of α-cumyl cations, which are based on the gas-phase basicity of α-methylstyrenes.[18,19] Very recently we have shown a surprisingly excellent linear relationship for the gas-phase stabilities of α-cumyl cations against the ordinary solution set of σ^+;[19] there seems to be no difficulty in defining a gas-phase σ^+ scale by this set of stabilities of substituted α-cumyl cations. Thus, the plot of the gas-phase stabilities of benzyl cations against α-cumyl cations in Fig. 2 corresponds to the gas-phase σ^+ plot of benzyl cation stabilities. We can clearly see that the substituent effect on the benzyl cation stability is intrinsically nonlinear to that on the α-cumyl cation stability, and that there is no common set of σ^+ constants for the gas phase carbocation stabilities. In this figure, a good linear relationship with a slope of unity is observed for meta and para π-acceptor substituents , whereas all para π-donor substituents significantly deviate upward from the line of unit slope. These deviations are systematic, and indicate a greater stabilization by the stronger para π-donor substituents. The deviation is just what would be expected for the system of an enhanced resonance demand. In fact, a close examination has revealed that the deviations of para π-donors can be accurately related to the resonance substituent parameter $\Delta\bar{\sigma}_R^+$ defined from solution phase reactivities. The LArSR theory can be equally applicable to treatment of the gas-phase substituent effects, and the benzyl cation should have an enhanced resonance demand in the intrinsic carbocation stability compared with that of the α-cumyl one. Most important, the r value derived from the gas-phase benzyl cation stability has been found to be identical with the value observed for the k_c solvolysis of the activated substituent range of benzyl tosylates. Evidently, the enhanced resonance demand (r=1.28) obtained in the benzyl solvolysis must be an intrinsic feature characterizing the nature of the transition state of k_c solvolysis of benzyl tosylate, rather than a correlational artifact of the nonlinearity caused from mechanistic complexity.

The exalted r value is not due to the k_s—k_c mechanistic shift as suggested by Shorter,[10] but to the enhanced resonance stabilization of benzyl cation compared with α-cumyl cation. The less stable primary benzyl cation should have an inherent resonance demand distinctly higher than the value of r=1.0 of tertiary α-cumyl cation system.

LArSR Correlation for Benzyl k_c Solvolysis

Benzyl solvolysis has been established to accompany a significant mechanistic transition with substituent change and, in fact, neither LArSR nor the simple Brown σ^+ equation was capable of linearly describing the substituent effect of this reaction. While the nonlinearity in both treatments is caused from a mechanistic change, the enhanced resonance demand must be intrinsic of this system and independent of any mechanistic complexity. Accordingly, a further precise consideration is needed for an analysis of the substituent effect on this reaction. As described in a preceding paper,[20] the statistical significance of the r parameter can be examined most reasonably by following the change in the standard deviation of statistical fittings to Eq. 1 as a function of the r value without any constraint of the ρ value. Generally, the SD changes remarkably with the r value to give a significant minimum at the best-fit r, and even a minor deviation from the best-fit r causes a sharp increase in the SD value.

The dependences of the standard deviations on r are shown for typical substituent sets of this solvolysis in Fig. 3, where the solid curves refer to the unrestricted substituent sets including *m,p*-disubstituted derivatives, and the dotted curves refer to the sets consisting only of typical single substituents without disubstituted derivatives.

In the solid line series, curve 1 for the all substituents set (refers to set No. 1 in Table 2) is not shown in Fig. 3, but it is far out of scale in SD and has no significant minimum at the best-fit r value, suggesting the involvement of substrates reacting by the k_s route. Only for the electron donor-region does Eq. 1 satisfy the criterion of acceptable conformity. Set No. 7 for the more reactive region than 4-MeS-3-CN gives a quite satisfactory SD vs. r curve with a sharp wedge of

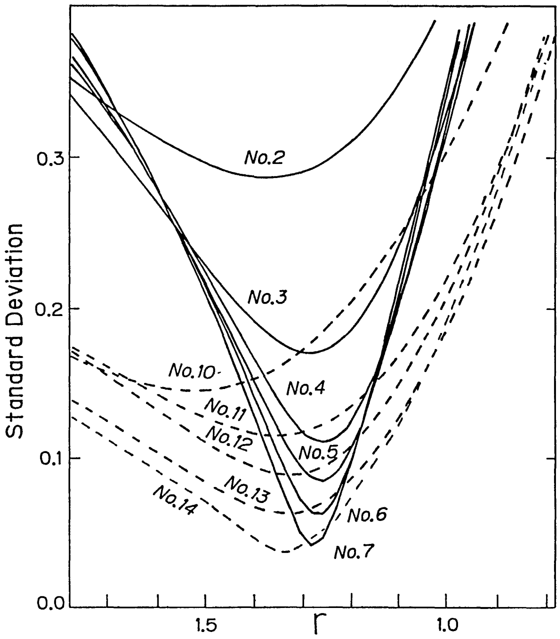

Fig. 3. The plot of SD against r for benzyl tosylates: The numbers refer to the set numbers in Table 2.

sufficient depth. No further significant change in the depth is observed, even if additional substituent points are further deleted. We can notice a significant difference in the broadness between solid and dotted curves. While the significant depth (small best-fit SD value) of the bottom should be the basic requirement for an acceptable correlation, the steepness is a direct measure of the reliability of the r value. The latter will be of particular importance for discussing the validity of the resonance demand for the k_c mechanism of this reaction.

In the dotted-line series consisting only of simple para π-donors without disubstituted ones, set No. 10 shows a considerably improved correlation with a higher r value without giving any deep minimum. While the LArSR analysis of these sets may result in even a better correlation than the corresponding σ^+ correlations, the minimum SD points in these sets are all above the precision level of acceptable conformity. The higher r value in these cases should be not completely free from the nonlinearity due to the k_c—k_s-mechanistic change. For attaining the precision of acceptable conformity, the LArSR Eq. should be applied to a more severely limited range of substituents, e.g., set No. 7, down to 4-MeS-3-CN group which likely refers to those reacting by a fixed k_c mechanism characteristic of benzyl system. Whereas the mechanistic complexity may often be an important cause of the failure of linear free energy relationships, it is never the actual cause of finding an enhanced r value in the k_c solvolysis of this system.

It is worthy of particular note that set No. 14 consisting of only single π-donors gives a similarly accurate best-fit LArSR correlation of comparable depth with the corresponding set No. 7 covering the same range of substituents but it gives an appreciably broader curve of low convergency. The best-fit r value for this set is slightly different from the value given by the solid-line sets, but has essentially no statistical significance, because of the flat basin of the SD vs. r plot. Set No. 10 gives a more accurate best-fit correlation of a smaller SD value than does set No. 3, but the latter gives a much steeper curve of significant convergency than the former. This may be a typical case where the better correlation is not always a reliable one and, indeed, reflects just what was particularly cautioned by Shorter.[10] Clearly, the steepness at the bottom and, hence, the validity of the correlation, depends appreciably upon the combination of substituents.

For typical para π-donor substituents of common use, there is an intrinsic close-linearity between the Brown σ^+ constants and $\Delta\bar{\sigma}^{+}_{R}$.[8] In a comparison between the LArSR and Brown σ^+ analyses, the nonlinearity of both parameters should be considered severely. The stronger p-π-donors are localized at the most reactive end in the σ^+ plot and tend to deviate significantly only at that end responding to the r value of the system, resulting in a concave plot indiscernible from the curvature caused by mechanistic transition. Such a curve break may become significant or even serious in the reaction having significantly different r value from unity. It should be emphasized that the use of the Brown σ^+ scale will have to be the only cause of a curve break for many systems having significantly different resonance demands, even without any mechanistic transition.[1] The behavior of strong π-donor substituents of less negative σ^+ values disturbing the σ^+ vs. $\Delta\bar{\sigma}^{+}_{R}$ linearity are most important in order to distinguish the real cause of the nonlinear σ^+ plot.[8] In the present study, we have utilized m-chloro- or m-cyano-substituted strong p-π-donors as such particular substituents, and their importance in an accurate estimation of the r value is clearly demonstrated by the remarkable difference in the sharpness between the solid and dotted series of SD vs. r curves.

Experimental

Materials: Substituted benzyl alcohols were prepared mostly from the corresponding esters by reduction with $LiAlH_4$. 3-Cyano-4-methoxy- and 3-cyano-4-methylthiobenzyl alcohols were prepared from the corresponding 3-bromo derivatives by the reaction with copper(I) cyanide in DMF.

Benzyl tosylates were prepared mostly by the Schotten-Bauman method according to a procedure mentioned in the literature.[15] The physical constants are summarized in Table 3.

The solvent 80% aqueous acetone for the solvolysis run was prepared by mixing the quoted volumes of acetone and water at 25 °C.

Table 3. Physical Properties of Benzyl Tosylates[a]

Subst.	Mp(decomp)/°C (lit. mp/°C)	H/%	C/% (Calcd)	N/%
p-MeS	Below r.t.			
p-PhO	95—97			
2-Fluorenyl	86			
2-Naphthyl	57.5—58.5			
4-MeS-3-Br	80.0—84.5	3.96	46.70	
		(3.90	46.52)	
4-MeS-3-Cl	89—91	4.42	52.62	
		(4.41	52.55)	
4-Me-3-Cl	58.7—59.1 (59.5—60.5)[b]			
3,4,5-Me$_3$	39(decomp)	6.71	66.75	
		(6.62	67.08)	
3,4-Me$_2$	40(decomp)	6.26	66.04	
		(6.25	66.18)	
3,5-Me$_2$	61.3—62.3	6.25	66.15	
		(6.25	66.18)	
p-Me	53.0 (57.9—58.5,[c] 49.5—50.5)[b]	5.89	65.15	
		(5.84	65.19)	
m-Me	60.0—60.8 (65.1—65.5,[c] 60.5—61.5)[b]	5.86	65.30	
		(5.84	65.19)	
p-Et	ca. 15 °C	6.26	65.84	
		(6.25	66.18)	
p-*i*-Pr	29—30.5	6.63	66.89	
		(6.62	67.08)	
p-*t*-Bu	55.2—56.1	7.04	67.87	
		(6.96	67.89)	
4-MeO-3-CN	92—101	4.73	60.55	4.33
		(4.76	60.55	4.41)
4-MeS-3-CN	76.8—77.1	4.53	57.04	4.22
		(4.53	57.64	4.20)
p-Ph	107—112 (114)[d]	5.34	71.00	
		(5.36	70.98)	
m-MeO	79.0—81.5 (83.7—84.0)[c]	5.53	61.65	
		(5.52	61.63)	
p-F	56.0—56.8 (56.2—56.7,[c] 54—55,[f]	4.77	60.06	
	48.5—52.5)[g]	(4.67	59.98)	
m-F	54—54.5 (54.2—54.7)[e]	4.68	59.91	
H	57.3—58.2 (58.5—58.9,[c] 58—59,[b]	5.46	64.05	
	54—56)[g]	(5.38	64.10)	
p-Cl	50.5—51.0 (53.0—53.5,[e] 51.6—53.0,[g]	4.40	56.53	
	52.3)[g]	(4.42	56.66)	
m-Cl	81.3—82.0 (81.5—82,[e] 80.5—81.5,[b]	4.47	56.67	
	80—81,[g] 81—83)[g]	(4.42	56.66)	
p-Br	74.7—75.9 (76.8—77.5,[c] 74.8—75.2)[e]	3.83	49.20	
		(3.84	49.28)	
m-Br	103.0—103.8 (105.2—105.6,[c]	3.92	49.37	
	102.3—102.6)[e]	(3.84	49.28)	
m-CN	67.8—68.1	4.71	62.80	
		(4.56	62.70	4.87)
p-CN	73—74	4.51	62.70	4.77
m-CF$_3$	66.2—67.0 (61—63)[g]	4.22	54.58	
		(3.97	54.54)	
p-CF$_3$	60—61	4.01	54.50	
p-NO$_2$	102.7—103.4 (105.0—105.5)[c]	4.32	54.81	4.54
		(4.26	54.72	4.56)
3,5-(CF$_3$)$_2$	79.3—80.1	3.03	48.28	
		(3.04	48.25)	

a) Tosylates (*p*-MeS, *p*-PhO, 4-MeO-3-Cl, 2-fluorenyl, and 2-naphthyl) were mostly not sufficiently stable to be isolated nor to be subjected to microanalysis. The melting points were only approximate ones because of the rapid decomposition. b)Ref. 14b. c) Ref. 21. d) Ref. 22. e) Ref. 13b. f) Ref. 13c. g) Ref. 15.

Rate Measurement: Solvolyses were followed conductometrically as described before.[1,8,9,23] Conductance measurements were made in a cell with bright platinum electrodes using approximately 25 or 50 ml of 10^{-3}—10^{-4} mol dm^{-3} solution in the thermostated bath at appropriate temperature controlled within ±0.01 °C. The rate determination at high temperature was carried out by the ordinary titration of generated toluenesulfonic acid at the initial concentration of 0.02 mol dm^{-3} starting tosylates using usual sealed ampoule technique as described before,[3] and also by using ampoule technique with conductivity determination.[8] The experimental errors in respective runs were generally less than 1.0% and rate constants from repeated runs were reproducible within an accuracy of 1.5%.

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