Substituent Effects. XVIII.[1] The Resonance Demand in the Acetolysis of Neophyl Brosylates

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The substituent effect in the acetolysis of neophyl brosylates was analyzed statistically based on the Yukawa-Tsuno LArSR equation. Though the Brown $\rho^+\sigma^+$ equation did not provide a linear correlation, the LArSR equation gave an excellent linear correlation with an r value of 0.57, substantiating our basic LArSR concept of varying resonance demands with different systems. For a statistical examination of the reliability of this nonunity r value, the change in the standard deviation of the LArSR correlation was followed as a function of varying r by an iterative least-squares method. The r value of the neophyl solvolysis must have sufficient statistical significance to distinguish between the LArSR and simple Brown $\rho^+\sigma^+$ correlations of this system. The significance of the best-fit correlation was found to strongly depend upon the number and combination as well as the range of the effective substituents. The study was extended to various aryl-assisted processes of complex mechanisms, solvolyses of 2-arylethyl, 2-aryl-1-methylethyl, 2-aryl-1-methylpropyl, and (1-arylcyclobutyl)methyl arenesulfonates. A precise dissection analysis of non-crossover k_Δ and k_s processes has been realized by the Gauss-Newton type nonlinear least-squares method based on the assumption of LArSR correlations for both processes. The generality of the unique r_Δ value of neophyl solvolysis was verified regarding these β-aryl-assisted processes. The substituent effect on the k_Δ process can be characterized far more appropriately in terms of the $\bar{\sigma}_\Delta$ of r=0.6, rather than σ^+ of r=1.00.

In the reactions of substituted phenyl derivatives, where a direct π-interaction between an aryl and a carbocationic center is possible, the substituent effect can generally be described by the Yukawa-Tsuno LArSR equation,[2-4]

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

The r value is a parameter of the resonance demand, i.e., the degree of resonance interaction between the aryl and the reaction site in the rate-determining transition state.

In the general application of Eq. 1, the 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 system (1-methyl-1-phenylethyl system) ($0<r<1$), but also to be significantly higher than unity ($r>1$) in many cases. 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.[3-9]

The substituent effect on the acetolysis of neophyl brosylates (2-methyl-2-phenylpropyl p-bromobenzenesulfonates) (**1**) was analyzed earlier in terms of our LArSR equation, giving an r value of 0.57.[5] This unique r value was reasonably referred to as a special mode of π-delocalization in the transition state, different from that of the solvolysis of α-cumyl chlorides.[5]

While the results of wide applications of Eq. 1 have provided strong support for our basic concept of varying demands of resonance effects for different systems,[3-5,8] contrary views have also been presented against the significance of the r value as a measure of resonance demands.[9-11] Most of these criticisms appear to arise primarily from the relatively small change of the r value in most benzylic solvolyses.[9] We have already pointed out that the σ^+ equation may be practically applicable to reactions having an r value within the range from 0.8 to 1.2.[4a] A definite answer to such criticisms will be provided by exploring the substituent effects on systems with r values significantly differing from unity, or from zero. Thus, we have analyzed the substituent effect in a highly electron-deficient solvolysis system, such as 1-aryl-1-(trifluoromethyl)ethyl tosylates, giving an extremely high r value of 1.39.[12] On the other hand, neophyl solvolysis would be appropriate, because of its r value, for an examination of the significance of the resonance demand r value in the range between σ^0 and σ^+; i.e., $0<r<1.0$.

An important criticism raised against the LArSR concept is that the deviation of r from unity or from zero may be caused in most cases by the complexity of the reaction mechanism.[9-11] The validity of the interpretation of the substituent effect relies on the mechanistic simplicity of the reaction. It is generally agreed that the solvolysis of neophyl brosylate proceeds through a rate-determining aryl-assisted transition state which immediately cascades downward to the tertiary carbenium ion.[13,14] The rate of this solvolysis reflects the aryl-assisted ionization step, and is not complicated either by an internal return or by nucleophilic solvent assistance.[14]

In the present study, we have carried out a detailed analysis of the substituent effect on neophyl solvolysis by using an extensive and statistically more significant data set. The purpose of this study was to confirm the validity of the LArSR concept of varying resonance demands and to assess the real reliability of the r value. The resonance demand of the neophyl solvolysis occupies an important position just intermediate between σ and σ^+ in the r scale. In order to realize our concept of the continuous spectrum of resonance demand, it appears to be necessary to confirm that a considerable body of aryl-assisted solvolyses should have characteristic resonance demands in this unique range of r scale. Thus, our study has been extended to various aryl-assisted processes of complex mechanisms, solvolyses of 2-arylethyl (**2**), 2-aryl-1-methylethyl (**3**), 2-aryl-1-methylpropyl (**4**), and (1-arylcyclobutyl)methyl arenesulfonates (**5**) in order to examine the generality of the neophyl r_Δ value in these aryl-assisted processes.

Results

The rate data of acetolysis of neophyl brosylates and substituent parameters are listed in Table 1. The substituent parameters employed in the present analysis are mostly the standard values.[4,5] In the present study, essentially no account was taken of the solvent-modification of substituent parameters in an acetic acid solution, whereas the substituent parameters of some particular substituents are known to be sensitive to solvent change.[5b,6] Acetic acid is also a rather special solvent and the hydrogen-bonding interaction of acidic solvent with a basic substituent, such as methoxy and methylthio groups, has frequently been pointed out as being important.[6] Particularly, the downward deviation of the *p*-methoxy group in the σ^+ plot for relevant β-aryl-assisted solvolyses in acidic solvents has been interpreted in terms of this fact.[6] However, this interpretation does not apply to the present acetolysis, since the same deviation behavior has been observed even for the σ^+ plot in nonacidic aqueous organic solvents,[6,17a] and no sizable deviations of any particular substituents have been observed in LArSR correlation using unmodified, standard substituent parameters. The substituent parameters of ordinary substituents are generally constant within less than ±0.02 in this solvent, as well as in many ordinary aqueous organic solvents. The σ^+ values for *m*,*p*-disubstituted derivatives were derived primarily from the solvolysis of the corresponding α-cumyl chlorides.[4b] Their definition is based on the combined effects of two substituents as a unified substituent in our treatment. The $\Delta\bar{\sigma}_R^+$ parameters given for these groups are the best average values to fit most LArSR correlations, and the σ^0 values are tentatively

Table 1. Acetolysis Rates of Neophyl Brosylates at 75 °C and Substituent Parameters

Subst.	$10^5k/\mathrm{s}^{-1}$[a]	$(k/k_0)_{75\,°\mathrm{C}}$	σ^0	σ_p^+	$\Delta\bar{\sigma}_R^+$
4-OCH_2CH_2-3[b]	1664[c]	242.6	−0.19	−0.94[d]	−0.75
4-MeO-3-Me	1187[c]	173	−0.18	−0.88	−0.70
p-MeO	582[c]	84.8	−0.100	−0.80	−0.70
p-C_6H_5O	96.8[c]	14.11	0.063	−0.54	−0.602
3,4,5-Me_3	169.4	24.69	−0.262	−0.449	−0.187
3,4-Me_2	103.5	15.09	−0.193	−0.38	−0.187
p-MeS	71.4[c]	10.41	0.12	−0.59	−0.71
p-Me	50.13[e]	7.31	−0.124	−0.311	−0.187
p-*t*-Bu	46.3	6.75	−0.155	−0.255	−0.100
4-MeO-3-Cl	32.7	4.77	0.22	−0.47[f]	−0.69
3,5-Me_2	24.83	3.62	−0.138		
p-C_6H_5	16.68	2.431	0.039	−0.20	−0.24
m-Me	13.18[g]	1.927[h]	−0.069		
H	6.86[i]	1.000	0.000	0.000	0.000
4-MeS-3-Cl	5.70	0.831	0.44	−0.28[f]	−0.72
p-F	5.376	0.784	0.20	−0.064	−0.264
4-MeO-3-CN	3.79	0.552	0.48	−0.21[f]	−0.69
m-MeO	4.531	0.661	0.05		
p-Cl	1.418	0.2067	0.281	0.115	−0.166
p-Br	1.09[g]	0.1594[h]	0.296	0.150	−0.146
4-MeS-3-CN	0.637	0.0929	0.68	−0.020[f]	−0.70
m-F	0.2575	0.0369[j]	0.352[k]		
m-Cl	0.221[c]	0.0318[j]	0.400[k]		
m-Br	0.2054	0.0296[j]	0.405[k]		
p-COOMe	0.132[g]	0.0189[h,j]	0.46		0.00
3,4-Cl_2	0.0898[c]	0.0128[j]	0.59	0.424[f]	−0.166
m-CN	0.0305[c]	0.00415[j]	0.615		
p-CN	0.0191[l]	0.00251[h,j]	0.670		0.00
p-NO_2	0.00760[l]	0.00080[h,j]	0.810		0.00

a) Data taken from previous papers (Ref. 5). b) 2-Methyl-2-(2,3-dihydrobenzofuran-5-yl)propyl brosylate. c) Extrapolated from the rate constants at other temperatures. d) Ref. 19. e) $49.7\times10^{-5}\,\mathrm{s}^{-1}$ in Ref. 18. f) Determined directly from α-cumyl solvolysis (Ref. 4b). g) Data taken from Ref. 18. h) Based on $6.84\times10^{-5}\,\mathrm{s}^{-1}$ for the unsubstituted derivative, Ref. 18. i) $6.84\times10^{-5}\,\mathrm{s}^{-1}$ in Ref. 18. j) Corrected for aryl-assisted rate based on product analysis data (see Ref. 5b). k) σ_m^+ values rather than σ_m^0. l) Ref. 20.

Table 2. Results of Correlation Analysis

No.	Substituent set	Correlation	n[a]	ρ	r	SD[b]	R[c]
1	All	LArSR	29	−3.828±0.023	0.578	0.038	0.9997
		σ^+	29	−3.051±0.135	(1.00)	0.332	0.9746
		σ	29	−4.234±0.197	(0.26)	0.349	0.9720
		σ^0	29	−4.136±0.405	(0.00)	0.672	0.8915
2	p-(−R)[d]	LArSR	18	−3.793±0.031	0.577	0.037	0.9995
		σ^+	18	−3.080±0.236	(1.00)	0.354	0.9559
3	All but disubst.[e]	LArSR	24	−3.850±0.031	0.567	0.040	0.9997
		σ^+	24	−3.087±0.109	(1.00)	0.257	0.9867
		σ	24	−4.422±0.158	(0.26)	0.261	0.9862
4	Mono-subst.[f]	LArSR	10	−3.702±0.052	0.614	0.025	0.9999
		σ^+	10	−2.871±0.108	(1.00)	0.154	0.9944
5	Electron donors[g]	LArSR	14	−3.854±0.076	0.566	0.036	0.9989
		σ^+	14	−2.296±0.225	(1.00)	0.241	0.9467
		σ	14	−4.579±0.742	(0.26)	0.366	0.8719
6	Limited typical electron donors[h]	LArSR	8	−3.677±0.097	0.606	0.023	0.9997
		σ^+	8	−2.393±0.148	(1.00)	0.133	0.9887
7	Meta, p-(+R)[i]	σ^0	11	−3.864±0.037	0.00	0.037	0.9996

a) Numbers of substituents involved. b) Standard deviation. c) Correlation coefficient. d) Para π-donors including disubstituted ones. e) Excluded 4-MeO-3-Cl, 4-MeO-3-CN, 4-MeS-3-Cl, 4-MeS-3-CN, and 3,4-Cl_2. f) A set of typical (mono-)substituents of which σ^0 and $\Delta\bar{\sigma}_R^+$ are roughly linear; 4-OCH_2CH_2-3, p-MeO, p-PhO, p-Me, H, p-F, p-Cl, p-Br, m-Cl, and m-Br. g) Substrates more reactive than unsubstituted derivative including H. h) Typical (mono-substituted) electron donors; 4-OCH_2CH_2-3, p-MeO, p-PhO, p-Me, p-t-Bu, p-Ph, m-Me, and H. i) Meta substituents and p-π-acceptor ones.

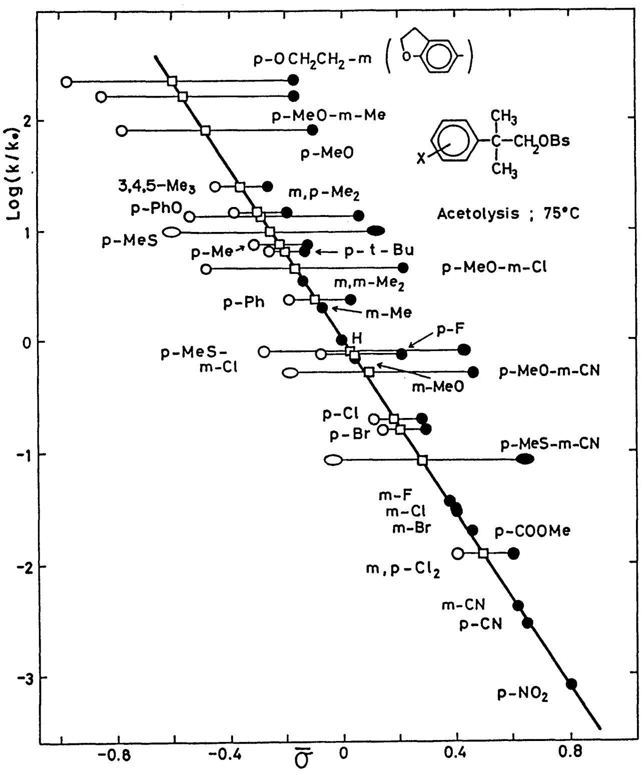

Fig. 1. The LArSR plot for the acetolysis of **1**; open circles σ^+, closed σ^0, and squares $\bar{\sigma}$ for r=0.57.

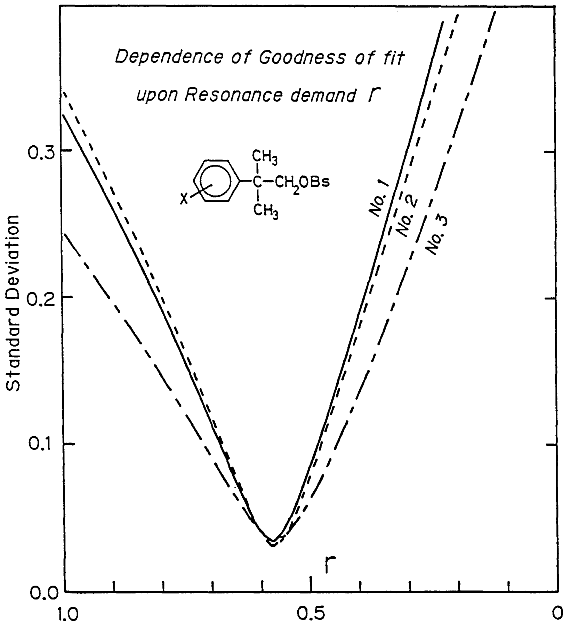

Fig. 2. The plot of SD as a function of r for the solvolysis of **1**: The numbers refer to the set numbers in Table 2.

given as the differences of $\sigma^+ - \Delta\bar{\sigma}_R^+$.

A correlation analysis was carried out using the substituent parameters given in Table 1 by an ordinary least-squares procedure; based on Eq. 1, in comparison with the simple Brown $\rho^+\sigma^+$ equation. The results are summarized in Table 2 and an LArSR plot for all substituents is shown in Fig. 1.

The accuracy of the LArSR correlation is higher than that of the σ^+ correlation by a significant factor of one decimal figure in the standard deviation for $\log(k/k_0)$. The SD values of ca. ±0.04 for LArSR correlations may be regarded as being nearly the ultimate precision attainable with linear substituent effect analysis for the set of $|\rho| \geqq 4$; thus, a detailed comparison of minor changes in SD below this level does not seem to be very meaningful.

In order to assess the validity of the LArSR analysis as well as the essential reliability of the LArSR correlation of this system, the change in the goodness of the fit to Eq. 1 was followed statistically as a function of varying r values without constraint for the ρ value by the iterative least-squares method. The results are shown graphically in Figs. 2 and 3.

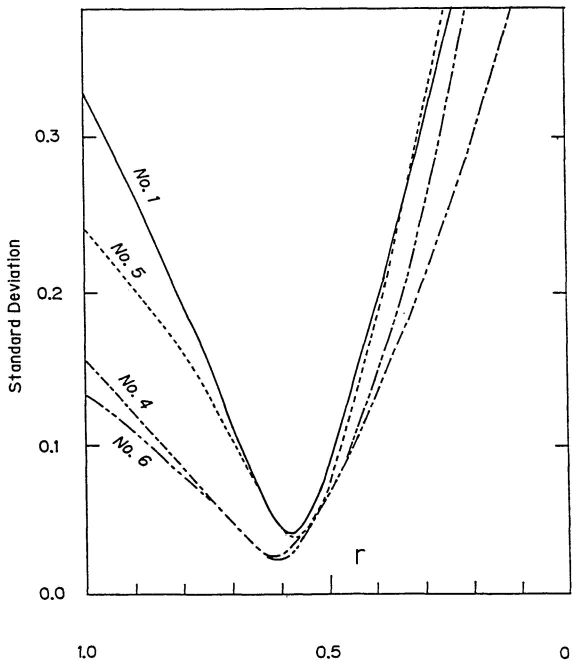

Fig. 3. The plot of SD as a function of r for the solvolysis of **1**: The numbers refer to the set numbers in Table 2.

Discussion

As described in the foregoing papers,[5] the essential features of the substituent effect on this system are clearly displayed by the LArSR plot in Fig. 1. *m*-Substituents and para π-acceptors satisfy a linear Hammett relationship, the range of which (ca. 10^4 in reactivity) is sufficiently wide to define the ρ_m correlation. For all substituents, the σ^+ correlation appears to be only fair, or even poor. The σ^+ plot (open circle) exhibits wide dispersion and splits into three parallel lines with significant gaps, for strong para π-donors, for weak para π-donors (alkyl and halogens), and for resonance-invariant substituents. Obviously, the $\sigma^+\rho^+$ treatment fails in giving a single linear correlation for all classes of substituents with satisfactory precision. In contrast, the LArSR plot with an r value of 0.57 is very linear. The horizontal line segments between σ^+ and σ^0 values for para π-donor substituents reflect the resonance capabilities of these substituents, i.e., $\Delta\bar{\sigma}_R^+$ values. The meta correlation line intersects all of the resonance segments at the points giving a constant ratio which refers to the r value (r=0.57) of this system.

The varied contribution of the resonance effect can be taken into account, as a precise approximation, by the application of Eq. 1, from which it immediately follows that

$$\bar{\sigma} = (\log k/k_0)/\rho = \sigma^0 + r\Delta\bar{\sigma}_R^+. \qquad (2)$$

This indicates that the exaltation of apparent $\bar{\sigma}_p$ from σ^0, the quantities $(\log k/k_0)/\rho - \sigma^0$, should be proportional to the resonance parameter $\Delta\bar{\sigma}_R^+$. Figure 4 illustrates such a plot of the linear resonance free energy relationship. The slope of 0.57 should corre-

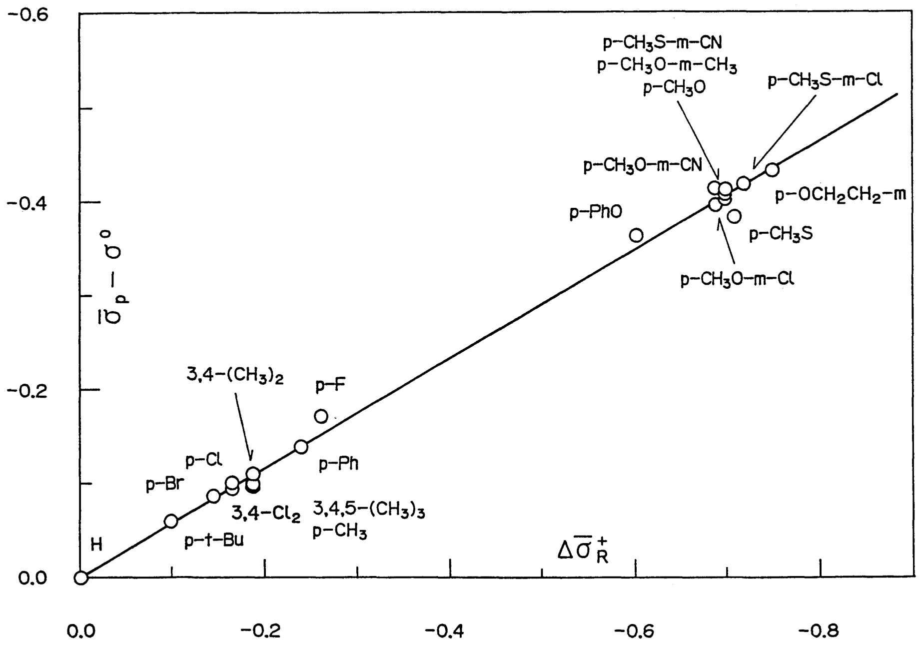

Fig. 4. The plot of the $(\log k/k_0)/\rho - \sigma^0$ against $\Delta\bar{\sigma}_R^+$.

spond to the r value of this reaction. It is obvious that there is no trend of curvature nor a significant deviation of particular substituents in the plot.

In Table 2 the LArSR ρ values for all sets are identical to the ρ_m value, and the LArSR r value remains constant within ±0.02. There is no particular class of substituents which cause any significant loss in the goodness of the fit. Particularly, the para π-donor set (No. 2) results in an identical LArSR correlation with that for set No. 1 with essentially the same precision, even without meta and π-accepting para substituents. From a comparison between the correlations for No. 3 and No. 1 sets, it is apparent that *m,p*-disubstituted derivatives also satisfy the same relationship without any significant loss of precision.

While the σ^+ values for two groups in *m,p*-disubstituted derivatives are not exactly additive, as is usually assumed, the effects are successfully accounted for in terms of the characteristic σ^0 and $\Delta\bar{\sigma}_R^+$ parameters defined for the combined effects of two substituents as a united substituent, in which the meta substituent is effective mainly in modifying the inductive effect of the overall system, and the $\Delta\bar{\sigma}_R^+$ values remain as essentially unchanged as those of the parent *p*-substituents.

The results of the LArSR analysis are consistent with the presently accepted mechanism of this reaction.[5,13,14] The substituent effect on the solvolysis rate should be concerned only with the aryl-assisted ionization step and, therefore, an r value of 0.57 is characteristic of this step. The exalted r value may be rationalized in terms of a direct π-interaction between the aryl π-system and the β-carbocation center at the rate-determining transition state and, in turn, suggests that a considerable positive charge is delocalized into the β-aryl ring; however, the delocalization is appreciably less effective in this reaction than in the α-cumyl solvolysis. The large ρ value is also in line with the bridged structure of the transition state.

A remarkable difference in the goodness of the fit by a factor of one order of magnitude in SD between the Brown σ^+ and our LArSR treatments lends support for the preference of our LArSR relationship. Nevertheless, it is often pointed out that an improved correlation may arise simply as a result of an increased number of parameters.[9,10]

The real significance of the r parameter in the LArSR correlation is most clearly illustrated in Figs. 2 and 3, which display the change of the standard deviation (SD) in the least-squares fitting to Eq. 1, as a function of r without constraint for the ρ value. Solid curve 1 shows the dependence of SD on r for a set involving all substituents (No. 1 in Table 2). 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. The depth and steepness of the wedge around the bottom, the most probable r point, may be indicative of the real reliability of the LArSR correlation. The sufficient depth is a basic requirement for an acceptable conformity, and the steepness is a direct measure of the reliability of the r value. It should be mentioned that the para π-donor set (No. 2) results in an identical SD vs. r plot of significant convergency at the same minimal point, even without meta and π-accepting para substituents which are capable of determining the ρ value most effectively. On the other hand, set No. 4, consisting only of typical substituents of common use, gives an even deeper minimum SD, but a slightly broader SD vs. r curve. Clearly, it can be seen that the steepness near the bottom, hence the reliability of r, depends appreciably upon the constituting substituents in the set, though the depth constantly and readily achieves a sufficiently small value for all sets.

Considering the accuracy of the substituent constants, any LArSR correlation should have an inevitable uncertainty which depends primarily upon the size of ρ and r of the reaction. From a general survey, the LArSR correlation is found to be generally accurate to ca. 0.015, or better than 0.02 in σ scale, at least for the solvolyses of established mechanistic simplicity. A reference SD level of acceptable conformity to the LArSR Eq. 1 of this reaction ($\rho\cong-4$) should be of the order of ±0.06—0.08 in SD. Further, the best-fit LArSR correlations for all of the substituent sets in Table 2 have higher precision, and detailed consideration of the change in the SD value below a level of ±0.06 appears not to be very meaningful. From the width of the SD vs. r plot at the reference level of SD=±0.06 of acceptable conformity, the r value for the all substituents set (No. 1) may be considered to be quite reliable within an estimated accuracy of the order of ±0.04. We will have to estimate a relatively large uncertainty limit of ca. ±0.08 in r value for set No. 4, consisting only of single substituents of common use. These accuracy values are considerably large in magnitude compared with the ordinary precision indices, and they should be appropriate for a relative comparison, though the absolute values may be only a qualitative measure. Even if such a large possible uncertainty is taken into account, the r value of this system should be reliable enough to be distinguished from a value of unity for the correlation with σ^+ and from 0.26 for the correlation with σ.

We now apply the LArSR analysis to the relevant solvolyses of β-arylalkyl arenesulfonates. A precise analysis of the substituent effects on most β-arylalkyl solvolyses, however, suffers from serious difficulties arising from a mechanistic complication caused by a competing solvent-assisted k_s process.[6,8,15] For sufficiently deactivating substituents, no aryl participation is observed, and the compounds react exclusively by the aryl-unassisted process (in most cases the k_s process). On the other hand, sufficiently electron-releasing substituents facilitate participation and such compounds react predominantly by the aryl-assisted

(k_Δ) process.

A useful way to separate the rates of the aryl-assisted process from the overall k_t (=k_Δ+k_s) has been exploited by Schleyer et al.,[6] based on the assumption of Hammett-type relationships for the respective pathways, practically observable in extreme cases, $k_\Delta \gg k_s$ and $k_s \gg k_\Delta$:[16]

$$\log(k_t^X/k_t^H) = \rho_s\bar{\sigma}_s + \log(k_s^H/k_t^H) \text{ for } k_s \text{ process } (k_s \gg k_\Delta)$$

and

$$\log(k_t^X/k_t^H) = \rho_\Delta\bar{\sigma}_\Delta + \log(k_\Delta^H/k_t^H) \text{ for } k_\Delta \text{ process } (k_\Delta \gg k_s),$$

where $\bar{\sigma}_\Delta$ and $\bar{\sigma}_s$ are the appropriate sets of substituent constants for the k_Δ and k_s processes, respectively.

For such complicated solvolysis processes, a precise dissection analysis into two independent processes has been realized[8,17] by the Gauss–Newton type nonlinear least-squares method based on the assumption of LArSR correlations for both k_Δ and k_s processes, as

$$k_t^X = k_\Delta^H 10^{\rho_\Delta(\sigma^\circ + r_\Delta\Delta\bar{\sigma}_R^+)} + k_s^H 10^{\rho_s(\sigma^\circ + r_s\Delta\bar{\sigma}_R^+)}, \tag{3}$$

where the first term on the right-hand side corresponds to the LArSR correlation for the k_Δ process[16] and the second to the correlation for the k_s process. The treatment is simplified by assuming that r_s for the k_s reaction can be fixed at zero for reducing a variable. The LArSR correlations derived in this manner for these k_Δ solvolyses are summarized in Table 3.

The combined correlation based on Eq. 3 reproduces the $\log(k_t^X/k_t^H)$ values with excellent precision, comparable with that of the correlation of neophyl solvolysis. The ρ_Δ values for the β-aryl-assisted k_Δ processes in all of these β-arylalkyl acetolyses are nearly identical with that for the neophyl solvolysis; the relatively large values, as for the neophyl value, indicate the generation of highly charged transition states. However, the ρ_s values are different from the ρ_Δ values and change significantly with the systems, reflecting the nature of their aryl-unassisted processes. The r_Δ values for these k_Δ processes are also nearly identical to the value for the neophyl acetolysis. Unfortunately, the LArSR correlations of the aryl-assisted k_Δ processes in these solvolyses are based on a limited range of substituents, in many cases only upon electron-donor substituents. It is most serious that in all of these sets any *m*-substituents reacting predominantly by the k_s mechanism are ineffective in the determination of either the r_Δ value or the ρ_Δ line for the k_Δ process. The reliability of the r_Δ value given for the respective systems cannot be estimated simply by the overall SD value. The statistical significance of the k_Δ correlation relies strongly upon the number and combination, as well as the range of the effective k_Δ substrates. The data points of dominant k_Δ substrates involved in these sets are equivalent to those in set No. 5 of neophyl solvolysis in Table 2.

Since it is generally agreed that the neophyl solvolysis proceeds through an exclusive k_Δ process, the above reliability analysis, the dependence of the correlation upon the selected substituents sets, allows an assessment of the actual reliability of the LArSR correlations for the k_Δ processes in these complicated β-arylalkyl solvolysis systems.

In Fig. 3, set No. 5, consisting of electron donor substituents (more reactive than the unsubstituted one), gives an SD vs. r plot of identical depth and steepness, as well as identical ρ and r values to those of the full substituents set (No. 1). On the other hand, either set No. 4 or a more limited set (No. 6) involving no electron acceptor substituents gives even a better correlation, but a much broader SD vs. r curve with a bowl shape. The best-fit r values in these sets (Nos. 4 and 6 in Table 2) should be much less reliable because of the essentially flat basin of their SD curves.

The range of constituting substituents in sets Nos. 4—6 is equivalent to the range covered by the dominant k_Δ substrate points in β-arylalkyl solvolysis systems given in Table 3.[17] As suggested by the identical convergence of curve No. 5 with that of the all substituents set (No. 1) in Fig. 3, the substituents constituting set No. 5 appear to satisfy the minimal substituent points required to achieve reliable LArSR k_Δ correlations of these solvolyses. Thus, the r_Δ values assigned to these solvolyses based on such substituent sets could be statistically distinguished from unity for α-cumyl solvolysis. It therefore appears likely that the substituent effect on the β-aryl-assisted process can be characterized by this common r_Δ value. In a dissection analysis into k_Δ and k_s processes by Eq. 3, the treatment can be much simplified by assuming a fixed r_Δ value at 0.57, as observed for neophyl solvolysis. This is essentially identical with the dissection analysis carried out by Schleyer et al.[6] for 2-arylethyl (**2**) and 2-aryl-1-methylethyl (**3**) systems.

Table 3. LArSR Correlations for Aryl-assisted Solvolyses in Acetic Acid

ROArs	Temp/°C	ρ_Δ	r_Δ	ρ_s	SD	$\log k_s^H/Fk_\Delta^H$
Neophyl OBs (**1**)	75	−3.83	0.58	—	0.038	—
2-Arylethyl OTs[a] (**2**)	115	−3.96	0.62	−0.19	0.035	0.48
2-Aryl-1-methylethyl OTs[b] (**3**)	100	−3.53	0.54	−0.81	0.025	0.52
threo-2-Aryl-1-methylpropyl OBs[c] (**4**)	75	−3.32	0.56	−1.07	0.042	−0.58
(1-Arylcyclobutyl)methyl OBs[d] (**5**)	55	−3.27	0.55	−1.16	0.050	0.44

a) Ref. 8. b) Ref. 17. c) Unpublished results in this laboratory and Ref. 21. d) Unpublished results in this laboratory and Ref. 22.

In their original dissection, Schleyer et al. employed the Brown σ^+ constants (i.e., r=1.00) for the k_Δ correlation,[23] whereas the result was not very successful. The p-methoxy group is in most cases the only substituent which has a particularly large $\Delta\bar{\sigma}_R^+$ value, compared with ordinary substituents, alkyl and halogens. The best-fit k_Δ correlation should, thus, be determined most effectively by the p-methoxy group. Because of the absolutely small ρ_s value, any possible correction for the k_s contribution could not bring about significant changes in the $\log k/k_0$ of the distinctly activated p-methoxy derivative. The statistical procedure by Eq. 3 determines the best-fit r_Δ value, and an application of iterative analysis using σ^+ with a fixed r_Δ value for the k_Δ does not appear to be very meaningful. In fact, they later reported a much better result of dissection with neophyl $\bar{\sigma}_\Delta$ values, instead of with σ^+ for the k_Δ correlation.[6] There is no doubt that the substituent effect on the k_Δ process is characterized far more appropriately in terms of a $\bar{\sigma}_\Delta$ of r=0.6 rather than σ^+ of r=1.00.

The results of the present LArSR analysis lead to the generalization that the r parameter shows little variation within a family of reactions proceeding essentially by the same mechanism, giving a unique r value characteristic of the transition state. The $\bar{\sigma}_\Delta$ value determined from the neophyl solvolysis can be applicable as a common set of substituent constants to a large body of β-aryl-assisted k_Δ solvolysis processes. This is exactly the same approach as that used by Brown when he introduced the σ^+ constant as a conventional substituent constant applicable to solvolyses of benzylic substrates. This requirement of a new set of substituent constants $\bar{\sigma}_\Delta$ with $r\approx0.6$ is consistent with our concept of a continuous spectrum of varying resonance demand.

Brown and Kim demonstrated in their first communication that the solvolysis of 2-aryl-1-methylpropyl brosylates (**4**) was linearly correlated with the Brown σ^+ without a significant break.[21a] This is rather serious, since a completely linear σ^+ correlation argues against any contribution of the competing k_s process. A fixed k_Δ mechanism for the whole substituent range is clearly inconsistent with the stereochemical result of the product analysis.[21] Similarly, Roberts reported a linear σ^+ plot for the solvolysis of (1-arylcyclobutyl)methyl brosylates (**5**), with a ρ^+ value of -1.0 (correlation coefficient 0.98).[22] The sign of this ρ value suggested a direct interaction between the substituents and the developing cationic center in the acetolysis transition state; however, the magnitude of ρ^+ was significantly lower than the ρ value for the acetolysis of neophyl brosylates, suggesting a limited charge delocalization into the aryl substituent in the transition state. Consequently, Roberts concluded that the k_Δ process involving an aryl-bridged species as the first-formed rate-controlling intermediate was unlikely. Instead, some other process involving cyclobutyl participation was considered to be consistent with these results.[22] It should be noted that there is a strictly linear relationship between the $\log k/k_0$ values for the solvolyses of **4** and **5**. The solvolysis of **4** involves a $k_\Delta - k_s$ mechanistic shift with substituents.[21] Again, these difficulties may arise primarily from the fortuitous conformity to the Brown $\sigma^+\rho^+$ relationship, which should indicate an operation of a single k_Δ mechanism for the whole substituent range of solvolysis of **5**. Thus, the simple Brown $\sigma^+\rho^+$ treatment, assuming a fixed r value, applies practically to these systems, whereas it appears to be incapable of providing a correct interpretation for the mechanistic details.

Finally, these results provide an answer to the suggestion that the deviation of r from unity or zero may be caused by the mechanistic complexity of the system.[9-11] The established simplicity is, indeed, the most important reason why we have chosen neophyl solvolysis for the present reexamination. Neophyl brosylate solvolyzes via a rate-determining aryl-assisted transition state and the reaction must not be complicated either by internal return or by nucleophilic solvent assistance.[5,13,14] On the other hand, the aryl-assisted k_Δ processes in the other relevant solvolyses in Table 3 are complex processes involving significant internal return.[6,8,15,17,21-23] The essential identity of r_Δ values for all these β-aryl-assisted processes indicates that the r_Δ value is characteristic of the common rate-determining k_Δ transition state, i.e., to be determined only by the rate of aryl-assisted ionization independent of return. This fact strongly argues against the general interpretation of a non-unity r value in terms of the mechanistic complexity of the reaction.[9-11]

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