VARYING RESONANCE DEMANDS IN SUBSTITUENT EFFECTS.
ACETOLYSIS OF NEOPHYL p-BROMOBENZENESULFONATES

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Abstract – Rates of acetolysis of 2-aryl-2-methylpropyl p-bromo-
benzenesulfonates were determined for an extended series of
substituents. The substituent effect can be described accurately
in terms of our LArSR relationship (Yukawa–Tsuno Equation),
giving an r value of 0.57.   The correlation result can be
reasonably accounted for on the basis of the accepted mechanism
of this reaction, involving a rate-determining aryl-assisted
transition state.   The present study leads to the conclusion
that this unique r value should be related to the resonance
demand characteristic of the aryl-assisted ionization process
of this reaction.   The simple application of the Brown $\rho\sigma^+$
equation or its extended treatment and the interpretation based
thereon are criticized.

In an earlier paper,[1] we pointed out that the substituent effect on the
acetolysis of neophyl brosylates[2] was described most reasonably with our original
LArSR[1] equation but not with the simple σ^+ treatment, and emphasized that the
unique r value could be referred to the different mode of resonance stabilization
of the transition state from that of cumyl chloride solvolysis.   The LArSR
analysis has been applied to the neighboring aryl-assisted solvolyses, to give in
most cases comparable r values with that for neophyl solvolysis.[3-5] What we have
envisaged in the LArSR Eq.[6,7] is to introduce the concept of varying resonance
demands of reactions into the substituent effect analysis.

$$\log \ (k/k_o) \ = \ \rho(\sigma^o + r\Delta\overline{\sigma}_R^+) \tag{1}$$

In other words, r is a parameter reflecting the different charge delocalization
into aryl ring at the transition state.[7] This permits evaluation of the nature
of the transition state, and has been widely applied to the assignment of reaction
mechanisms, for solvolyses,[7,8] aromatic substitutions,[7] and neighboring aryl
assisted reactions.[1,3]

   However, a contrary view has also been presented against the significance of
the r value as a measure of resonance demands.[9] This view essentially stands on
the assumption of a fixed resonance demand (r=1) for conjugative carbocation
reactions, supported by the broad applicability of the σ^+ treatment.[10] It appears
necessary to   reexamine whether our basic LArSR concept of varying demands on
resonance effects with different systems is valid.   The point of the contrary
view is that the deviation of r from unity or zero should be attributed for most
cases to the complexity of the reaction mechanism.[9,11,12] Thus the validity of

the observed r value as the resonance demand rests heavily upon the validity of the mechanism or the mechanistic simplicity of the system employed. Neophyl solvolysis is an appropriate model for the aryl-assisted process, simple as far as the rate-determining transition state is concerned, and uncomplicated by either internal return or nucleophilic solvent assistance.[4,13-16] Further, in order to statistically differentiate between the LArSR and simple σ^+ correlations, the neophyl acetolysis giving a unique r value significantly different from unity or zero, would be most appropriate for this reexamination. Accordingly, in the present study, we have determined the acetolysis rates of neophyl brosylates for an extended series of substituents and carried out a detailed analysis of the substituent effect in terms of Eq. (1).

Results

The rate constants of acetolyses of neophyl brosylates for an extended set of substituents were determined, according to the ordinary titrimetric method.[1b,2,3b] The rates were generally in satisfactory agreement with literature values.[2] The rate data are summarized in Table 1, together with those available in the literature. Tanida et al.[17] pointed out earlier that the solvolysis of the p-nitro derivative involved a competing methyl migration. Gas chromatographic analysis of the solvolysis products indicated detectable methyl migration with deactivated derivatives. The methyl-migration rates (in Table 2) for those derivatives were derived based on the aryl/methyl migration ratios. The rate of methyl migration was less sensitive to the aryl substituents to give a small ρ value of ca. -0.6 ∿ -0.7, and essentially no methyl-migration was found with more activated compounds than m-halo-ones. The rates for the p-CN and the p-COOMe derivatives were estimated based on the substituent-dependence ($\rho \doteq -0.6$) of the methyl-migration rates of other derivatives. The aryl-assisted rates were corrected for methyl-migration. However, for the remarkable divergence of solvolysis rates with substituent the minor errors involved in the correction are not considered to affect the following discussion of the substituent effect on the aryl-assisted process.

The substituent parameters employed in the present analysis are mostly the standard values (Table 3). In the present analysis no special account has been taken for the solvent-modification of substituent parameters in acetic acid solution. For m,p-disubstituted derivatives, the σ^+ values were determined directly from the solvolysis of the corresponding cumyl chlorides:[8] The definition is based on the combined effects of two substituents as a unified substituent. The $\Delta\bar{\sigma}_R^+$ parameters given for these groups are the average values best for general LArSR correlations, and the σ^0 values are defined as the differences of $\sigma^+ - \Delta\bar{\sigma}_R^+$.

The correlational analysis based on Eq. (1), in comparison with Brown's $\rho^+\sigma^+$ analysis has been carried out using these sets of substituent parameters by the ordinary least squares procedure. The results are summarized in Table 4.

Meta substituents inclusive of para π-acceptors give an excellent correlation against standard σ^0 values. The σ^+ correlation for all substituents appears to be only fair or even poor and the ρ^+ value differs from the above ρ_m value. The partial σ^+ correlation for only the para π-donors (set No. 4) is similarly poor, suggesting no possibility of an independent linear correlation for p-π-donors.

On the other hand, the LArSR analysis affords excellent correlations for all sets. The ρ values for LArSR correlations are all identical to the ρ_m, and the r

values are constant within ±0.01 for all sets. It is remarkable that all the LArSR correlations show distinctly improved precision by an order of magnitude in SD compared with the σ^+ correlations. The SD values $\leq\pm0.04$ for LArSR correlations, equivalent to the uncertainty of 8 – 9% in rate constants, are considered to be nearly an ultimate precision attainable with linear substituent effect analysis for the set of $|\rho| \geq 4$, given the best accuracy of 0.005 for the substituent constants. There is no particular class of substituents causing any significant

Table 1. Acetolysis of neophyl brosylates

Subst.	Temp.($^{\circ}$C)	$10^5 k (s^{-1})$	$(k/k_o)_{75^{\circ}C}$	$\Delta H^+_{75^{\circ}C}$ (kcal/mol)	$\Delta S^+_{75^{\circ}C}$ (e.u.)
p-OCH$_2$CH$_2$-m	25	6.33±0.03			
	35	22.9±0.2			
	45	72.2±0.4			
	75	1664[a]	242.6	22.2	-3.1
p-MeO-m-Me	25	4.25±0.01			
	35	15.37±0.09			
	45	49.9±0.1			
	75	1187[a]	173	22.5	-3.0
p-MeO	25	1.921±0.023			
	35	7.17±0.04			
	40	13.00±0.11[b]			
	45	23.32±0.06			
	50	42.2±0.3			
	55	72.79±0.31			
	75	582[a]	84.8	22.8	-3.5
p-C$_6$H$_5$O	50	6.68±0.03			
	60	20.22±0.06			
	70	58.7±0.4			
	75	96.8[a]	14.11	23.3	-5.9
m,p-Me$_2$	75	103.5±0.6	15.09		
p-MeS	45	2.52±0.002			
	60	14.47±0.005			
	70	42.6±0.4			
	75	71.4[a]	10.41	23.8	-4.7
p-Me	75	50.13±0.1[c]	7.31		
p-t-Bu	75	46.3±0.3	6.75		
p-MeO-m-Cl	75	32.7±0.1	4.77		
m,m-Me$_2$	75	24.83±0.1	3.62		
p-C$_6$H$_5$	75	16.68±0.04	2.431		
m-Me	75	13.18[d]	1.927[e]		
H	75	6.86±0.01[f]	1.000		
p-MeS-m-Cl	75	5.70±0.02	0.831		
p-F	75	5.376±0.030	0.784		
p-MeO-m-CN	75	3.79±0.01	0.552		
m-MeO	75	4.531±0.007	0.661		
p-Cl	75	1.418±0.005	0.2067		
p-Br	75	1.09[d]	0.1594[e]		
p-MeS-m-CN	75	0.637±0.002	0.0929		
m-F	75	0.2575±0.0007	0.0369[g]		
m-Cl	90	1.144±0.003			
	115	13.32±0.09			
	75	0.221[a]	0.0318[g]	26.8	-7.7
m-Br	75	0.2054±0.0003	0.0296[g]		
p-COOMe	75	0.132[d]	0.0189[e,g]		
m,p-Cl$_2$	90	0.473±0.001			
	115	5.67±0.03			
	75	0.0898[a]	0.0128[g]	27.1	-8.6
m-CN	75	0.0305[a]	0.00415[g]	27.4	-10.0
	90	0.163±0.001			
	115	2.00±0.02			
p-CN	75	0.0191[h]	0.00251[e,g]		
p-NO$_2$	75	0.00760[h]	0.00080[e,g]		

a) Extrapolated from the rate constants at other temperatures.   b) $13.2\times10^{-5}s^{-1}$ given in ref. 18.   c) $49.7\times10^{-5}s^{-1}$ in ref. 2.   d) Data taken from ref. 2.   e) Based on $6.84\times10^{-5}s^{-1}$ for the unsubstituted derivative, ref. 2.   f) $6.84\times10^{-5}s^{-1}$ in ref. 2 ; $6.99\times10^{-5}s^{-1}$ in ref. 18.   g) Corrected for aryl-assisted rate based on product analysis data, see Table 2.   h) Ref. 17.

Table 2.   Acetolysis products of neophyl brosylates

X	Me-migration%	$10^5 k_t(s^{-1})$	$10^5 k^{Me}$	$10^5 k^{Ar}$
m-F	1.8±1.0	0.2575	0.0046	0.253
m-Cl	1.5±0.5	0.221	0.0033	0.218
m-Br	1.3±0.1	0.2054	0.00267	0.203
p-COOMe	—	0.132[a]	0.0025[c]	0.129
m,p-Cl$_2$	2.4	0.0898	0.0022	0.0876
m-CN	6.4	0.0305	0.00205	0.0285
p-CN	—[b]	0.0191[b]	0.0020[c]	0.0171
p-NO$_2$	25.4[b,d]	0.00760[b]	0.00193	0.0055

a) Ref. 2b.   b) Ref. 17.   c) Estimated from the Hammett relation for methyl-migration rates as $\rho=-0.6$.   d) k_s product, 2.4% and aryl-migration product, 72.2%.

loss in goodness of fit.   Comparison of No. 7 with No. 5 sets confirms that m,p-disubstituted derivatives satisfy the same relationship without loss of precision. The same LArSR correlation with identical precision for set No. 6 of only p-π-donors suggests that p-π-donors themselves will be capable of determining the LArSR ρ and r values, even without the aid of meta and π-acceptor para substituents.

Discussion

All the essential features of the correlation results are clearly illustrated in Fig. 1. Meta substituents and para π-acceptors give a linear relationship, the range of which ca. 10^4 in reactivity is wide enough to define the ρ_m correlation as a rigid reference common to both the σ$^+$ and LArSR analyses.   Despite earlier suggestion of an improved σ$^+$ correlation for this reaction,[2b] the present σ$^+$ correlation appears to be only fair or even poor.   The σ$^+$ plot (open circle) in Fig. 1 exhibits wide dispersion and splits into three separate parallel lines with significant gaps for strong para π-donors, weak ones (para alkyl and halo groups),

Table 3.   Substituent parameters

Substituent	σ_p^o	σ_m^o	σ_p^+	$\Delta\bar{\sigma}_R^+$
p-OCH$_2$CH$_2$-m	-0.19		-0.95[a]	-0.75
p-MeO-m-Me	-0.18		-0.88	-0.70
MeO	-0.100	0.05[b]	-0.80	-0.70
3,4-Me$_2$	-0.193	-0.138[c]	-0.38	-0.187
PhO	0.063		-0.5	-0.602
MeS	0.10		-0.60,-0.53[a]	-0.65
Me	-0.124	-0.069	-0.311	-0.187
t-Bu	-0.150		-0.250	-0.100
p-MeO-m-Cl	0.22		-0.47[d]	-0.69
Ph	0.039		-0.179[d]	-0.218
p-MeS-m-Cl	0.44		-0.29[d]	-0.73
F	0.20	0.352[e]	-0.07	-0.264
p-MeO-m-CN	0.48		-0.21[b,d]	-0.69
Cl	0.281	0.400[e]	0.115	-0.166
Br	0.296	0.405[e]	0.150	-0.146
p-MeS-m-CN	0.68		-0.02[b,d]	-0.70
COOMe	0.46			0.00
3,4-Cl$_2$	0.59		0.42[d]	-0.166
CN	0.670	0.615		0.00
NO$_2$	0.810			0.00

a) H.C.Brown, C.G.Rao, and M.Ravindranathan, J.Am.Chem.Soc., 99, 7663 (1977).
b) Slightly solvent dependent.   c) 3,5-Dimethyl.   d) Determined directly from cumyl solvolysis.   e) σ_m^+ values rather than σ_m^o.
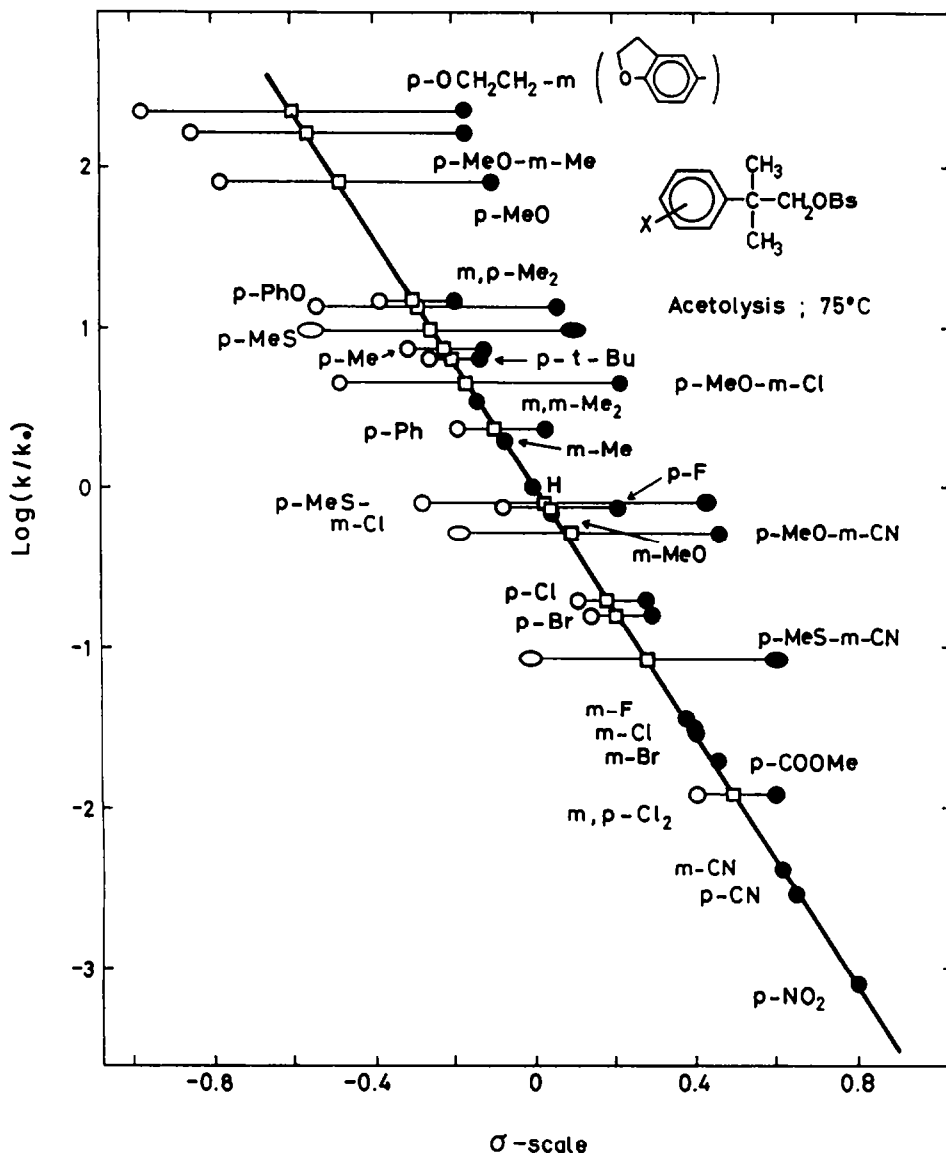
Fig. 1. LArSR plot for acetolysis of neophyl brosylates at 75°C:
Open circles σ^+, closed σ^0, and squares $\bar{\sigma}$ for r = 0.57.

and resonance-invariant substituents. Obviously, the $\rho^+\sigma^+$ treatment fails to give any single linear correlation or even single monotonically curved one for all classes of substituents with satisfactory precision. As a probable cause of significant deviations, the hydrogen-bonding interaction of acidic solvent with methoxy (inclusive of MeS) substituents was pointed out to be important in relevant aryl-assisted solvolyses.[16] However, this interpretation does not apply to the present acetolysis, since similar deviation behavior has been observed even for the σ^+ plot in non-acidic aqueous organic solvents,[19] and no sizable deviations of any particular substituents are observed in the LArSR correlation using unmodified, standard substituent parameters.

Table 4. Results of correlation analysis

No.	Correlation	Substituent Set	n^a	ρ	r	SD^b	R^c
1	σ^o	meta, p-(+R)^d	11	-3.864 ± 0.037	0.00	0.037	0.9996
2	σ_+	all	28	-4.287 ± 0.203	(0.26)	0.347	0.9721
3	σ^+	all	28	-3.036 ± 0.136	(1.00)	0.329	0.9750
4	σ^+	p-(-R)^e	17	-3.059 ± 0.232	(1.00)	0.345	0.9593
5	LArSR	all	28	-3.843 ± 0.022	0.576	0.035	0.9997
6	LArSR	p-(-R)^e	17	-3.814 ± 0.028	0.572	0.032	0.9997
7	LArSR	all but disubst.^{f}	23	-3.859 ± 0.030	0.569	0.037	0.9997

a) Number of substituents involved. b) Standard deviation. c) Correlation coefficient. d) All meta substituents inclusive of p-π-acceptors. e) p-π-Donors including disubstituted ones. f) Excluded p-MeO-m-Cl, p-MeO-m-CN, p-MeS-m-Cl, p-MeS-m-CN, and 3,4-Cl$_2$.

The excellent linear LArSR plot (squares) with an r value of 0.57 contrasts sharply with the poor one given by σ^+. Figure 1 most clearly explains the significance of r in the LArSR description of resonance effects as well as the way of change of apparent substituent constant with reaction. The stretches between σ^+ and σ^o values for para π-donor substituents represent their resonance capabilities, i.e., $\Delta\bar{\sigma}_R^+$ values. The ρ_m correlation line intersects all the stretches at the points giving a constant ratio which refers to the r value of this system. There seems to exist no other line intersecting all stretches at any other constant ratio. The LArSR correlation line can be readily found as a unique line intersecting at such a constant ratio for para π-donors stretches, even without aid of meta substituents. This is confirmed by the identity of LArSR correlations (5) and (6) in Table 4.

The results of the LArSR analysis are consistent with the presently accepted mechanism of this reaction. The reaction is considered to proceed through a rate-determining aryl-assisted transition state and cascade down to the tertiary carbonium ion,[4,20] presumably without staying as long-lived bridged intermediate. According to this mechanism, the substituent effect on the solvolysis rate should be concerned only with the aryl-assisted ionization step and therefore the r value of 0.57 is to be 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 considerable positive charge is delocalized into the β-aryl ring but the delocalization is appreciably less effective in this reaction than in the cumyl solvolysis. The large ρ value is also in line with the bridged structure of the transition state. For solvolyses of bicyclic systems, Grob[21] has accounted for the enhanced inductive effect ρ value for the substituents at assisting site in terms of the enhanced σ-bond participation. While an inductive (or field) effect ρ value depends appreciably upon the geometry, an exalted r value, implying enhanced π-interaction relative to inductive one, can be taken as much more clear-cut evidence for bridging in the transition state of the β-aryl solvolysis.

The precisely linear LArSR correlation may be indicative of the absence of any appreciable mechanistic change within the range of substituent change. On the other hand, the non-linear σ^+ correlation may be indicative of mechanistic change. The strictly linear ρ_m line defines the correlation for the wide-spread reactivity with a fixed mechanism, and all substituents should satisfy this correlation with an adequate $\bar{\sigma}_\Delta$ set in the absence of mechanistic change. In general, the mechanistic shift with effective substituent perturbation takes place favoring the

energetically preferred mechanism, and any substituted derivatives thereby reacting should exhibit higher reactivities than expected for the unperturbed mechanism defined by the meta correlation. This means that the mechanistic shift with substituents will always result in an upward concave plot against an adequate set of substituent constants. The way of deviations in the σ^+ plot in Fig. 1, seemingly a downward curvature, argues against any interpretation in terms of mechanistic change. Non-linear correlations are often interpreted in terms of non-linear response of the transition state stability to the electronic substituent perturbation, such as saturation effect. Quadratic expression or power series approximation in terms of an appropriate $\bar{\sigma}$ has been applied to such non-linear correlations: $\log (k/k_o) = \rho\bar{\sigma} + m\bar{\sigma}^2$.[22] Obviously, such a treatment with σ^+ as appropriate $\bar{\sigma}$ does not apply to the present system, since this equation can only account for a smooth-curved correlation but not a significant split one.

In summary, the r value of 0.57 may be referred to the resonance demand of the ionizing process with an aryl-assisted transition state. The resonance demand of this transition state is different from that of cumyl solvolysis. This is actually our conclusion from the present study and provides strong support for our LArSR concept of the varying resonance demands.

r Value and Mechanistic Complexity

The most important criticism against our LArSR concept is that the deviation of r from unity or zero should be attributed for most cases to the complexity of the reaction mechanism.[9] The reasonableness of interpretation relies upon the mechanistic simplicity of this reaction, and the established simplicity is indeed the most important reason why we have chosen this reaction for the present reexamination.

For the precise LArSR correlation, any acceptable interpretation should be based on the mechanism which accounts for complete conformity to the LArSR relationship of r = 0.57. Johnson suggested that the reaction conforming to the LArSR Eq. (1) with any intermediate r value is of two steps, a pre-equilibrium and a rate-determining step, one of which correlates with σ^o (or σ) and the other with σ^+.[9]

$$\log k/k_o = \rho_1\sigma^o + \rho_2\sigma^+ = (\rho_1 + \rho_2)(\sigma^o + \frac{\rho_2}{\rho_1 + \rho_2} \Delta\bar{\sigma}_R^+) \qquad (2)$$

This is formally equivalent to our LArSR Eq. (1) and capable of exactly reproducing the present excellent LArSR correlation.

On the other hand, as the LArSR Eq. (1) implies, the unified description of substituent constants in terms of varying r leads to a unique additivity relationship of substituent effects.

$$\log k/k_o = \Sigma\rho_j(\sigma^o + r_j\Delta\bar{\sigma}_R^+) = \rho'(\sigma^o + r'\Delta\bar{\sigma}_R^+) \qquad (3)$$
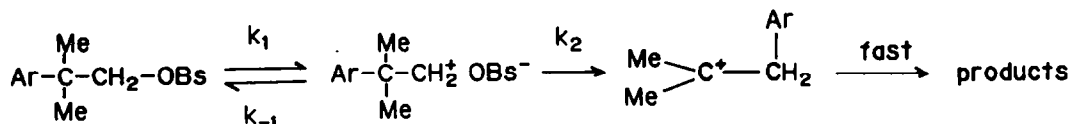
where $\rho' = \Sigma\rho_j$ and $r' = \Sigma\rho_j r_j/\Sigma\rho_j$. For the above pre-equilibrium mechanism, the overall substituent effect can be represented by Eq. (4), totally as a single linear LArSR correlation with an apparent r' value.

$$\log k/k_o = (\rho_1 + \rho_2)(\sigma^o + \frac{\rho_1 r_1 + \rho_2 r_2}{\rho_1 + \rho_2} \Delta\bar{\sigma}_R^+) \qquad (4)$$

Although the present analysis was essentially based on a priori assumption of $\rho_1 = \rho_\Delta$ and $\rho_2=0$ for the accepted mechanistic scheme, the Eq. (3) allows in theory to assign any reasonable r_j value for each step; since ρ_j's and r_j's are
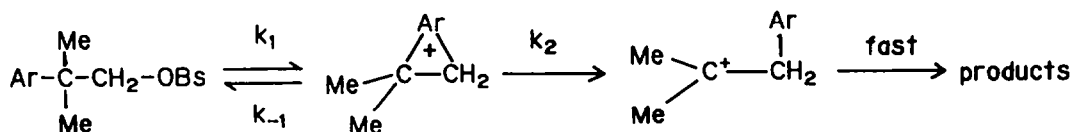
mathematically indefinite.   Clearly, Eq. (2) is a special case of r_1 = 0 and r_2 = 1.00, or vice versa, in Eq. (4) and noticeably, this specification enables us to unambiguously dissect the overall correlation to the composite ones for respective processes.   The examination of how Eq. (2) applies to the interpretation of the present result should be of particular value to clarify our position and to argue what we have envisiged in the LArSR Eq.

A conceivable, though not probable, multi-step mechanism is one involving the simple ionization to a primary carbocation followed by the rearrangement (aryl-assisted) process.   The former step may be referred to σ^0 and the latter to σ^+ term.   Brown et al. earlier described this process as cascading downhill in energy

$$Ar\text{-}\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{C}}\text{-}CH_2\text{-}OBs \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar\text{-}\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{C}}\text{-}CH_2^+ \ OBs^- \xrightarrow{k_2} \underset{Me}{\overset{Me}{>}}C^+\text{-}\overset{\overset{Ar}{|}}{CH_2} \xrightarrow{fast} products$$

from a highly unstable primary carbocation to a far more stable tertiary ion.[20] This mechanism, however, is not compatible with the present result, since it should result in the substituent effect of σ^0-dependence. To account for the enhanced r value, the second   step should be rate-determining, $k_{-1} \gg k_2$.   It seems however highly unlikely that the simple ionization (k_c) into an unstable primary ion occurs energetically so easily without aryl-assistance, compared with the rearrangement to a far more stable tertiary ion.[2,20] Furthermore, while Eq. (2) gives a definite ρ_1 value of -1.65, the methyl migration process which should proceed through a common ionization step with the aryl-migration one gave in fact a ρ value as small as -0.6 $\sim$ -0.7.

For the scheme, aryl-assisted ionization followed by effective decay process, the ionization process may be referred to σ^+, and the second step must necessarily

$$Ar\text{-}\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{C}}\text{-}CH_2\text{-}OBs \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Me\text{-}\overset{\overset{Ar}{\overset{+}{\diagup \backslash}}}{\underset{\underset{Me}{}}{C}}\text{-}CH_2 \xrightarrow{k_2} \underset{Me}{\overset{Me}{>}}C^+\text{-}\overset{\overset{Ar}{|}}{CH_2} \xrightarrow{fast} products$$

be referred to σ^0.   As far as the subsequent decay process is fast enough, $k_{-1} \ll k_2$, the overall substituent effect may be σ^+-dependent as assumed for the ionization step. When the second step is rate-determining, $k_{-1} \gg k_2$, the apparent substituent effect may be a blend of those on the ionization and decay processes. Only this mechanistic scheme may be capable of reasonably accounting for the non-unity r value.   However, note that the former single step mechanism for the case of $k_{-1} \ll k_2$ is in fact the presently accepted one for the neophyl solvolysis, and the latter mechanism of two steps of $k_{-1} > k_2$ is the accepted one for the k_Δ process of 2-arylethyl and 1-aryl-2-propyl acetolysis.[4,16] By this fact we mean that Eq. (2) can predict an intermediate r value for arylethyl or arylpropyl solvolysis but r of unity for the present neophyl one, or otherwise the well-accepted mechanisms should be incorrect. Even if the second step may be rate-determining, Eq. (2) would not simply be capable of giving any lower r value than unity, because the second step may have a positive ρ value inherent in either the attack of the nucleophile or the conversion from the bridged to open carbocation and the return from the intermediate should be essentially diffusion controlled (with ρ=0).[9b] Furthermore, there is no reasonable interpretation for a large negative ρ_2 of -1.65 given for the second step by Eq. (2).   Thus, in any case,

the Johnson scheme does not appear to apply to the present reaction. Most crucial is the fact that the pre-equilibrium ionization mechanism should involve significant return from the intermediate but many experimental facts suggest no significant return in this reaction.[23]

Equation (2) fails to interpret the present substituent effect based on the first aryl-assisted ionization mechanism and even leads to the denial of generally accepted mechanism. This inconsistency evidently arises from the unreasonable specification of two r_j's but not from the inadequacy of the pre-equilibrium scheme itself. Most β-aryl-assisted (k_Δ) solvolyses including neophyl solvolysis result in essentially the same apparent r value, regardless of appreciable changes in substrate structure and varying degrees of complexity in detailed mechanism.[1,3,4,16] This strongly argues for our previous conclusion that the unique intermediate r value must be characteristic of β-aryl-assisted ionization process. The assignment of this unique r for the aryl-assisted ionization step can provide reasonable interpretation for any accepted mechanisms of these solvolyses. For the neophyl solvolysis of essentially single step mechanism, the observed r' should be identical with the intrinsic r for the ionization, according to Eq. (3). For the 2-arylethyl solvolysis of two-steps one, the apparent r' may differ from but should not be lower than the r value for ionization. Nevertheless, as long as $|\rho_1|>|\rho_2|$ is valid, the overall r' value should be close to the intrinsic r value for the first ionization step. Furthermore, the r_2 for subsequent decay process should not necessarily be as low as r=0. Since the close-lying transition states should have electronically similar structures to the intermediate in the ordinary endothermic solvolysis processes, the r value for these processes will be all comparable to the r for the ionization process. Although we can not rule out the pre-equilibrium mechanism generally as a possible cause of varying r value, the interpretation as a blend of σ^+ and σ^0 relationships is not acceptable for the present system as well as most reactions giving non-unity r values.

Experimental

Material
Most of neophyl alcohols were prepared by the usual method by methylation of benzyl cyanides to α,α-dimethylacetonitriles,[24] followed by alkaline hydrolysis and LiAlH$_4$ reduction.
2-(p-Methoxy-m-cyanophenyl)-2-methyl-1-propanol was prepared from β-(p-methoxyphenyl)-isobutyric acid. Bromination of β-(p-methoxyphenyl)-isobutyric acid in acetic acid at 40-45°C to give β-(p-methoxy-m-bromophenyl)-isobutyric acid which was treated with LiAlH$_4$ in ether and immediately decomposed. Crude alcohol was fractionated to give pure p-MeO-m-Br-neophyl alcohol, which was converted into the m-CN alcohol by refluxing with CuCN in DMF for 3 h, according to Friedman and Shechter procedure,[25] and purified by SiO$_2$ column chromatography. p-Methylthio-m-cyanoneophyl alcohol was prepared in a similar way. p-Methoxy-m-chloroneophyl chloride was obtained from o-chloroanisole and methallyl chloride according to the direction for neophyl chloride;[26] bp 126-128°C/1 mmHg in 60% yield. Oxidation of the Grignard reagent gave p-MeO-m-Cl-neophyl alcohol.
Substituted neophyl p-bromobenzenesulfonates were prepared from corresponding neophyl alcohols by the Tipson procedure[27] with p-bromobenzenesulfonyl chloride in pyridine and purified by recrystallization from appropriate solvents.[1b]

Kinetic measurement
The acetolysis rates were measured by the titrimetric method using the usual ampoule technique as desribed before.[1b]

Product analysis
Acetic acid solutions (10 ml) of brosylates (0.02 M) in ampoules were allowed to react at 115°C. After ten half-lives each solution was diluted with water (100 ml) and extracted with CHCl$_3$. The extract was treated with aq. NaHCO$_3$, dried over MgSO$_4$ and evaporated. The composition of the residue was determined by GLC (DGS at 110 - 160°C) and confirmed by the retention time comparison with authentic samples.

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