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The Substituent Effects on Solvolyses of *threo*-2-Aryl-1-methylpropyl Brosylates

Mizue Fujio,* Naomi Goto, Tetsuro Dairokuno, Mutsuo Goto,
Yoshihiro Saeki, Yoshimi Okusako, and Yuho Tsuno
Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812

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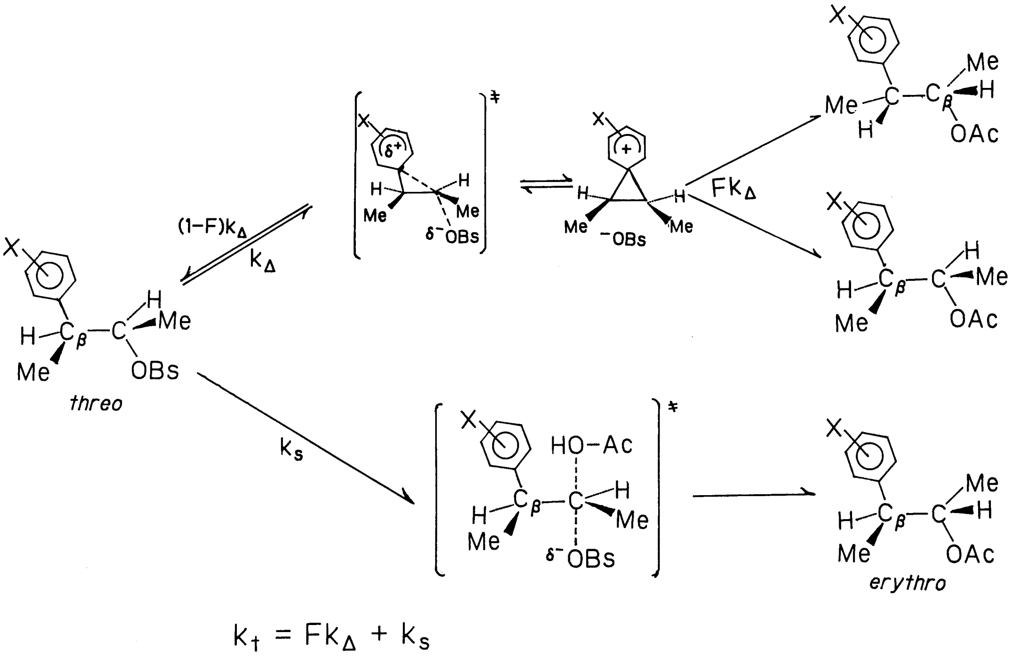
The solvolysis rates of *threo*-2-aryl-1-methylpropyl brosylates were determined for a series of substituents in acetic acid and 80% aq ethanol. The nonlinear substituent effect on the total rate was dissected with excellent precision into two linear LArSR relationships, each for the aryl-assisted (Fk_Δ) and unassisted (k_s) processes. The use of the Brown σ^+ for the dissection of the k_Δ-correlation of this system failed to give any satisfactory results. The intermediate resonance demand of the k_Δ solvolyses must be far beyond the scope of the Brown σ^+ treatment with a fixed resonance demand of unity. The ρ_Δ and r_Δ values for the k_Δ process of *threo*-2-aryl-1-methylpropyl solvolysis were given to be −3.36 and 0.56 in AcOH, and −3.71 and 0.54 in 80% aq EtOH, respectively; they were identical to those for other aryl-assisted solvolyses, such as the neophyl system. Regardless of the structures of the reaction site, the resonance demands of β-aryl-assisted solvolysis of an identical mechanism all fall within a narrow range of 0.5—0.6 in the r scale of the continuous spectrum of resonance demands in aryl-conjugating carbocation solvolyses. The resonance demand of the aryl-assisted k_Δ mechanism can be characterized in terms of this intermediate r value.

It has been established that the substituent effect on the β-aryl-assisted solvolysis process can be described in terms of the LArSR equation,[1]

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

generally with an intermediate r value characteristic of the aryl-assisted ionization process.[2–6] In our continuing studies on the aryl-assisted process we have been concerned so far mainly with detailed examinations of the structural effects in the primary β-arylalkyl systems. A structural change from the primary to the secondary reaction site may cause an appreciable perturbation in its mechanism, i.e., a considerable shift in the position of the transition state along the reaction coordinate of the aryl-assisted reaction process,[7–9] in addition to a certain enhancement in the reactivity. It appears interesting to examine whether the aryl-assisted solvolysis of the secondary system gives a unique intermediate r value similar to that of primary systems or not. The solvolysis of 2-aryl-1-methylpropyl benzenesulfonates is well-known as a representative secondary k_Δ system;[9–14] historically, the product stereochemistry of this solvolysis system led to Cram's first proposal regarding the intervention of a phenonium ion intermediate.[10a)]

Analyses of substituent effects on the aryl-assisted process often suffer from a mechanistic complexity caused by the concurring solvent-assisted process in addition to the return process from the phenonium intermediate (Scheme 1).[9] The solvolysis rate (k_t) corre-



$$k_t = Fk_\Delta + k_s$$

Scheme 1. Acetolysis mechanism of *threo*-2-phenyl-1- methylpropyl brosylate.

sponds to a sum of rates (k_s+Fk_Δ) of two competing processes, aryl-assisted (Fk_Δ) and unassisted (k_s) ones.[9] F is the fraction of the forward process forming the product(s) from the phenonium intermediate. Although the starting *threo* ester should give exclusively the *threo* product via the pathway of the aryl-assisted mechanism, it often is accompanied with the *erythro* product brought about by the aryl-unassisted k_s mechanism. Regarding the acetolysis of *threo*-2-aryl-1-methylpropyl brosylates (*p*-bromobenzenesulfonates), Brown once pointed out a good linear σ^+ relationship which implies the operation of a constant mechanism involving a direct aryl resonance interaction with the reaction site for the range of all substituents, whereas the complete linearity of the substituent effect on this solvolysis conflicted with the product analysis results, indicating the varying competition of two non-crossover (k_Δ and k_s) processes with a change in the aryl substituents.[11a] Thus, they unwillingly dealt with the k_Δ reactivity only as a discrepancy from the σ-correlation for the k_s process determined by the electron-attracting groups.[11] From this viewpoint, there have been no precise studies based on a correlation analysis of the substituent effect on the k_Δ process of this system.

In the competing k_Δ and k_s systems, no participation by aryl has been observed, and the compounds react through the unassisted (k_s) pathway when the substituents are sufficiently deactivating. On the other hand, sufficiently electron-releasing substituents facilitate participation and such compounds react predominantly by an aryl-assisted (Fk_Δ) pathway. The substituent effect on k_t ($=Fk_\Delta+k_s$) is given by

$$\log(k_t^X/k_t^H) = \log(k_s^X/k_s^H) + \log(1 + Fk_\Delta^X/k_s^X) + C_s$$

or

$$= \log(Fk_\Delta^X/Fk_\Delta^H) + \log(1 + k_s^X/Fk_\Delta^X) + C_\Delta,$$

where C_s and C_Δ are constants referring $\log(k_s^H/k_t^H)$ and $\log(Fk_\Delta^H/k_t^H)$, respectively. When the second terms on the right-hand side are neglected, a simple Hammett-type relation may be obtained with appropriate sets of substituent constants ($\bar{\sigma}_s$ and $\bar{\sigma}_\Delta$) for the k_s and Fk_Δ processes, respectively,

$$\log(k_t^X/k_t^H) = \rho_s\bar{\sigma}_s + C_s \quad \text{for extreme case of } k_s^X \gg Fk_\Delta^X$$

and

$$= \rho_\Delta\bar{\sigma}_\Delta + C_\Delta \quad \text{for the other extreme } Fk_\Delta^X \gg k_s^X.$$

However, Brown's substituent data covering the range from the *p*-MeO to the 3,5-(CF_3)$_2$ groups are still insufficient and inappropriate for our purpose to precisely define the two independent substituent effects and to estimate especially the resonance demand of the reaction center for an aryl-assisted (k_Δ) process based on LArSR Eq. 1. In this study we have extended the range of substituents of *threo*-2-aryl-1-methylpropyl brosylates sufficiently widely to make a comparison with the other primary β-arylalkyl system,[2–4] and analyzed the respective substituent effects on the k_s and Fk_Δ processes in terms of the LArSR Eq. 1.

Results and Discussion

The rate constants of the solvolyses of *threo*-2-aryl-1-methylpropyl brosylates were determined in glacial acetic acid titrimetrically and in 80% (v/v) aqueous ethanol (80EtOH) conductimetrically. The reproducibility of the rate constants from repeated runs was well within ±1%. The solvolysis rates are summarized in Table 1 together with those from the literature. Brown's k_t values for the unsubstituted and *p*-chloro derivatives in acetic acid are in precise agreement with ours within the experimental uncertainty; their acetolysis data for several derivative were also included without calibration in the present study.

The substituent effect on this solvolysis is displayed most clearly in Fig. 1, where the logarithms of the relative acetolysis rates are plotted against σ°, σ^+, and LArSR $\bar{\sigma}_\Delta$. Quite a similar behavior was observed for the substituent effect in 80EtOH at 45 °C. These plots do not satisfy any simple linear relationships at all with any single set of substituent constants. Brown and Kim pointed out a linear σ^+ correlation, with $\rho^+=-2.4$ at 25 °C in AcOH, based on a set of eight typical substituents (*p*-MeO, *p*-Me, *m*-Me, H, *p*-Cl, *m*-Cl, *m*-CF_3, and *p*-NO_2).[11a] They accidentally found a fortuitous conformity of the σ^+ values with a single minor deviation of that of *p*-Cl.

The key principle of our simple inspection is that only with appropriate $\bar{\sigma}_s$ and $\bar{\sigma}_\Delta$ substituent parameters will the apparent k_t plot result in a single monotonic curvature converging to the correlation lines at either the activating or deactivating end.[3,5] This permits the evaluation of the Fk_Δ and k_s correlations from the apparent k_t plot. Meta substituents and para π-acceptor substituents, where $\bar{\sigma}_s=\bar{\sigma}_\Delta=\sigma^\circ$ in electrophilic resonance reactions, can unequivocally define the nonlinear k_t correlation in terms of the standard σ° constants. In the Fig. 1, the k_t correlation curve (solid line) ranging from 3,5-(CF_3)$_2$ to 3,5-Me_2 should be a rigid reference for analyzing the behavior of *p*-π-donor substituents susceptible to the resonance demand. The k_t-correlation curve can be extrapolated to intersect the $\Delta\bar{\sigma}_R^+$ stretches at all the points to give a constant ratio close to 0.5, which refers to the r value of the k_Δ process. Most significant, the LArSR $\bar{\sigma}_\Delta$ plots (squares) all collapse into a single smooth curve determined by r-independent groups. The plot for the activating substrates is sufficiently linear to define the converging Fk_Δ correlation line with ρ_Δ values of about -3.5, as the tangent line for the k_t curve at the activating end. While the k_t curve intersects the line segments of *p*-Cl and *p*-Br substituents at points in between their $\bar{\sigma}_\Delta$ and

Table 1. Rate Constants of *threo*-2-Aryl-1-methylpropyl Brosylates

Subst.	AcOH$^{a)}$		80% aq EtOH$^{b)}$	
	Temp/°C	10^5k_t/s^{-1}	Temp/°C	10^5k_t/s^{-1}
4-OCH$_2$CH$_2$-3$^{c)}$	75.0	1330$^{d,e)}$	25.0	54.96
	45.0	92.0$^{d)}$	35.0	177.2
			45.0	530.8$^{f)}$
p-MeO	25.0	1.94, 1.95$^{g)}$	25.0	24.24
	45.0	24.7	45.0	233.8$^{j)}$
	75.0	649$^{h,i)}$		
2-Fl	75.0	151$^{d)}$	45.0	35.2
p-PhO	45.0	4.66	45.0	41.31
	65.0	43.0		
	75.0	119$^{h,k)}$		
3,4-Me$_2$	45.0	4.36	45.0	39.70
	65.0	41.5		
	75.0	116$^{h,l)}$		
p-MeS	75.0	99.1$^{h)}$	45.0	36.45
	65.0	35.71		
	45.0	3.824		
p-Me	75.0	81.4$^{h,m)}$	45.0	27.15
p-*t*-Bu	75.0	82.1	45.0	24.17
3,5-Me$_2$	75.0	40.24	45.0	12.31
m-Me	75.0	28.2$^{m)}$	45.0	7.677
4-MeO-3-Cl	75.0	49.8	45.0	13.22
H	45.0	0.460	45.0	5.780
	75.0	17.8,$^{n)}$ 18.0$^{m)}$		
p-F	75.0	11.32	45.0	4.073
4-MeS-3-Cl	75.0	11.09	45.0	2.636
p-Cl	75.0	4.291, 4.53$^{m)}$	45.0	1.429
m-Cl	75.0	2.05$^{m)}$	45.0	0.8328
p-Br	75.0	3.613	45.0	1.240
m-Br	75.0	1.955	45.0	0.8116
m-CF$_3$	75.0	1.38$^{m)}$	45.0	0.6031
p-CF$_3$	75.0	1.26$^{m)}$		
m-CN	75.0	0.9098	45.0	0.4897
p-CN	75.0	0.8091	45.0	0.4689$^{h,o)}$
			55.0	1.471
			75.0	11.89
p-NO$_2$	75.0	0.495$^{p)}$		
3,5-(CF$_3$)$_2$	75.0	0.330$^{m)}$		

a) Titrimetrically determined, otherwise noted. b) In volume. Conductimetrically determined. c) 2-(2,3-Dihydrobenzofuran-5-yl)-1-methylpropyl brosylate. d) By conductimetric method (less reliable; see experimental). e) $\Delta H^{\neq}=18.9$ kcal mol^{-1} and $\Delta S^{\neq}=-13.1$ e.u. (1 cal=4.184 J and 1 e.u.=4.184 J K^{-1} mol^{-1}). f) $\Delta H^{\neq}=20.7$ kcal mol^{-1} and $\Delta S^{\neq}=-3.9$ e.u. g) Ref. 12b. h) Calculated from other temperatures. i) $\Delta H^{\neq}=23.3$ kcal mol^{-1} and $\Delta S^{\neq}=-2.0$ e.u. j) $\Delta H^{\neq}=20.7$ kcal mol^{-1} and $\Delta S^{\neq}=-5.5$ e.u. k) $\Delta H^{\neq}=23.1$ kcal mol^{-1} and $\Delta S^{\neq}=-6.0$ e.u. l) $\Delta H^{\neq}=23.4$ kcal mol^{-1} and $\Delta S^{\neq}=-5.1$ e.u. m) Ref. 11. n) $\Delta H^{\neq}=26.1$ kcal mol^{-1} and $\Delta S^{\neq}=-1.0$ e.u. o) $\Delta H^{\neq}=23.1$ kcal mol^{-1} and $\Delta S^{\neq}=-10.5$ e.u. p) Ref. 11; estimated from tosylate reactivity in Ref. 10b.

σ° values in the mechanistic crossover region, this is just what is expected for an effective contribution from the concurrent k_s process of essentially σ°-dependence. On the other hand, neither the σ° nor σ^{+} plot gives any reasonable single Fk_{Δ} correlation line connecting smoothly to the k_t-curve. The LArSR $\bar{\sigma}_{\Delta}$ plots (squares) for the activating substrates all fall into a single smooth curve determined by the r-independent groups. The σ^{+} and LArSR $\bar{\sigma}_{\Delta}$ correlations are contrasted most sharply by the behavior of the less activating strong π-donors, such as 4-MeO-3-Cl and 4-MeS-3-Cl substituents. It is evident that an intermediate r value is the inevitable requirement in order to account for the substituent effect on the Fk_{Δ} process of the present reaction, as observed for the primary 2-arylethyl solvolysis.[2-4,6]

A precise correlation analysis of the substituent effect on the aryl-assisted (Fk_{Δ}) process has been achieved by an iterative nonlinear least-squares method described for the analysis of the acetolysis of 2-phenylethyl tosylates (*p*-toluenesulfonates).[3,7] Since the apparent rates are a sum of rates for two discrete pathways (Fk_{Δ} and k_s), which are described in terms of LArSR Eq. 1, the k_t rates are given by the following sum of two exponential functions:

$$k_t = Fk_{\Delta}^{\mathrm{H}}10^{\rho_{\Delta}(\sigma^{\circ}+r_{\Delta}\Delta\bar{\sigma}_{\mathrm{R}}^{+})} + k_{\mathrm{s}}^{\mathrm{H}}10^{\rho_{\mathrm{s}}(\sigma^{\circ}+r_{\mathrm{s}}\Delta\bar{\sigma}_{\mathrm{R}}^{+})}. \tag{2}$$

The substituent effect on the k_s process may be treated

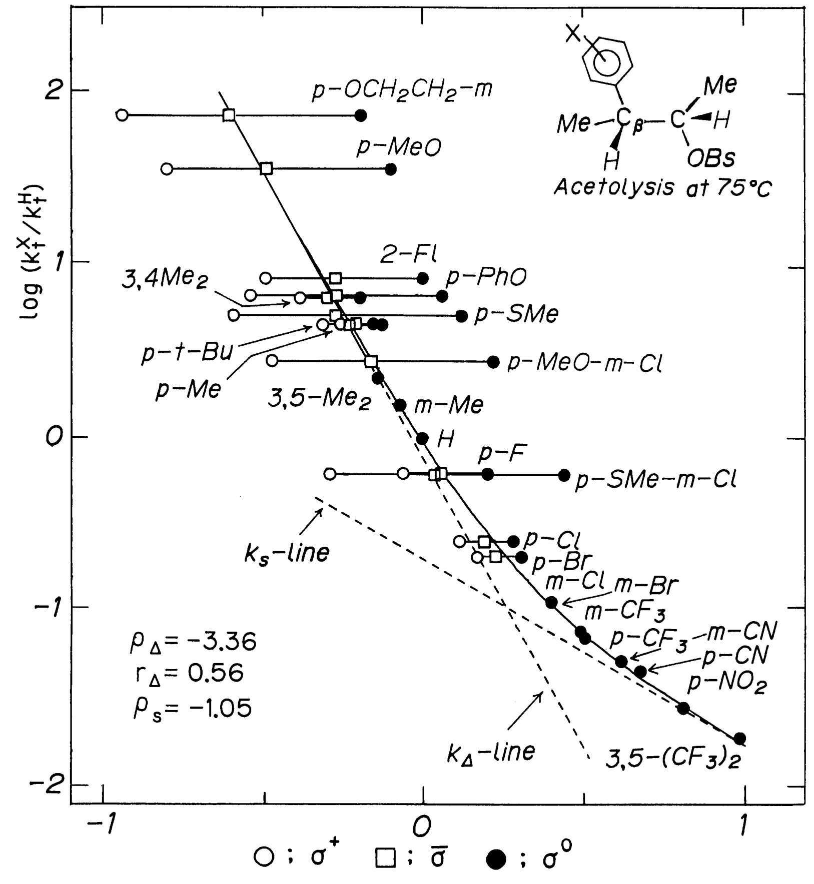


Fig. 1. LArSR plot for the acetolysis of *threo*-2-phenyl-1-methylpropyl brosylate; open circles σ^+, closed σ°, and squares $\bar{\sigma}$ for r=0.56.

Table 2. Substituent Effects on the Solvolysis of 2-Arylalkyl Arenesulfonates

Solv.	Temp/°C	ρ_Δ	r_Δ	ρ_s	SD[a]	Fk_Δ/k_s[b]
threo-2-Aryl-1-methylpropyl brosylates						
AcOH	75	−3.36±0.09	0.56±0.02	−1.05±0.12	±0.045	3.73
80E	45	−3.71±0.10	0.54±0.02	−0.75±0.20	±0.045	2.62
2-Aryl-1-methylethyl tosylates[c]						
AcOH	100	−3.53±0.10	0.54±0.02	−0.81±0.05	±0.025	0.305
80E	55	−3.81±0.16	0.58±0.02	−0.39±0.05	±0.034	0.124
Neophyl arenesulfonates						
AcOH[d]	75	−3.83±0.02	0.58±0.01		±0.038	
80E[e]	45	−3.97±0.07	0.56±0.03		±0.087	
2-Arylethyl tosylates[f]						
AcOH[f]	115	−3.96±0.10	0.62±0.01	−0.19±0.05	±0.035	0.330
50E[g]	65	−4.22±0.17	0.56±0.02	−0.18±0.03	±0.024	0.0349

a) Standard deviation in log-scale. b) Relative ratio of Fk_Δ and k_s for the unsubstituted derivative. c) Ref. 5. d) Ref. 2; brosylates. e) Ref. 5b; *m*-nitrobenzenesulfonates. f) Ref. 3. g) Refs. 7 and 32.

simply with σ° (i.e., r_s=0), since the process involves no direct π-interaction between the aryl and reaction site. The best-fit ρ_Δ, r_Δ, and ρ_s values are determined by a nonlinear least-squares method,[3-5,15] based on a minimization of the sum of the squares of the differences between the observed and calculated k_t values.[15b] In Fig. 1, Fk_Δ and k_s lines are drawn for the statistically best-fit correlations; they are in line with the above graphical examinations. Correlation results are shown in Table 2 in comparison with those for relevant 2-arylalkyl solvolyses.

Taking account of the different temperatures of the measurement, the ρ_Δ value of the 2-aryl-1-methylpropyl system differs negligibly between both solvents. It is worth noting that despite a different nucleophilicity between AcOH and 80EtOH, the ρ and r values in the LArSR correlation for the k_Δ process of 2-aryl-1-methylpropyl solvolysis are essentially unchanged with solvents, and are even identical to those observed in almost all k_Δ solvolyses, such as neophyl (2-methyl-2-phenylpropyl) solvolysis, as shown in Table 2.[2–6] This fact implies that the methyl substitution at the side chain does not affect the resonance demand in the aryl-assisted solvolysis process, and that the resonance demand for a series of reactions with a single mechanism should occupy a characteristic position of a narrow range in the r scale of the continuous spectrum of resonance demand.[6] Essentially, the aryl-assisted transition state can be characterized by this intermediate r value.

The difference in the substituent effect between secondary and primary systems is indeed significant in the unassisted (k_s) process, rather than in the k_Δ process. The ρ_s values of ca. -1 observed for the k_s process in the solvolysis of 2-aryl-1-methylpropyl brosylates (in both AcOH and 80EtOH) are comparable to those for 2-aryl-1-methylethyl tosylate,[5] but are much larger in magnitude than -0.2 for the solvolysis of primary 2-arylethyl tosylates.[3] The higher ρ_s value for secondary systems may be caused from an enhanced carbocationic character of the k_s mechanism of a secondary reaction center. Of course, the absolutely small ρ_s values for the k_s processes should be essential for the reaction at a remote β-position from the substituent aryl position. The appreciably lower ρ_s value in strongly nucleophilic aqueous EtOH, than in AcOH, is compatible with the higher nucleophilicity of the solvent in the former; namely, the cationic character of the reaction center may be reduced due to an enhanced bond-formation with a strongly nucleophilic solvent at the transition state in the aryl-unassisted secondary solvolysis.

In the neophyl solvolysis, the solvolysis rates are referred directly to the aryl-assisted ionization step without any complication by an internal return.[2,7,9,16,17] On the other hand, the aryl-assisted process of 2-aryl-1-methylpropyl brosylates is a complex one involving a significant internal return, at least in AcOH.[9,12–14] The essential identity of the r_Δ values for these aryl-assisted processes indicates that the r value should be determined only by the common rate-determining step of the first aryl-assisted ionization. This fact strongly argues against Johnson's generalized reasoning of intermediate r values in terms of the mechanistic complexity of the reaction.[18,19]

Brown's conclusion was that their results cannot be accommodated by a mechanism proposing a simultaneous formation or crossover of open (essentially limiting) and bridged ions, but the possibility that a rapidly equilibrating pair of open cations may be capable of controlling the stereochemistry of the product, achieving a predominant retention of the configuration without any request for the formation of a bridged intermediate (based on the kinetic approach of the small rate acceleration in the acetolysis of 2-phenyl-1-methylpropyl tosylate).[11c] The present result demonstrates that there is no significant difference with respect to the mode of the aryl π-charge delocalization in phenonium intermediates between the primary and secondary reaction site systems. This argues against Brown's conclusion that only weak participation[11c] comparable to the π-complex formation in the aromatic substitution could be operative in the present system between the reaction center and the β-aryl group; further, that there should be rapid equilibration between the pair of open cations.

The broad applicability of a single σ^+ scale, implying a fixed resonance demand (r=1.0), to most benzylic solvolyses generating stable tertiary carbocations[20] could result from the closeness of the resonance stabilization of solvolytic transition states. It is just the same situation that an intermediate (less than unity) r value is generally required to correlate the substituent effect on aryl-assisted reactions of various β-arylalkyl systems.

The results of the LArSR analysis are summarized for solvolyses of a series of conjugative aryl-substituted substrates in Table 3. The resonance demand in a benzylic series significantly increases as the developing carbocation is destabilized by benzylic substitution. Clearly, there is a continuous spectrum of varying resonance demands inherent in solvolyzing substrates, ranging from nonconjugative carbocation reactions (r=0.0) via the Hammett σ reactivities (r=0.26) and the so-called σ^+ category of r=1.00 to the extremely electron-deficient carbocation systems of $r \geqq 1.5$.[6] The r-values for the β-aryl-assisted solvolyses are at a characteristic position of r=0.5—0.6 in the spectrum of varying resonance demand. This unique intermediate r value can be attributed to the less effective π-delocalization through the β-

Table 3. LArSR Correlation for Benzylic Systems

Systems	In solution[a]		In gas-phase[b]	
	ρ	r	ρ[c]	r
Neophyl	−4.32[d]	0.57		
2-Phenylethyl	−3.96[e]	0.62	−12.8	0.60[f]
ArCMe$_2$	−4.59[g]	1.00	−9.5	1.00[h]
ArC(Me)H	−5.45[i]	1.15	−9.9	1.14[j]
ArCH$_2$	−5.23[k]	1.28	−10.2	1.29[l]
ArC(Me)CF$_3$	−6.29[m]	1.39	−10.2	1.40[n]
ArC(CF$_3$)H	−6.05[o]	1.53	−10.6	1.53[p]

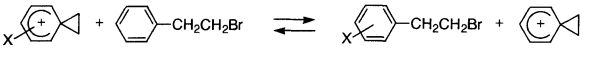
a) Derived from the solvolysis of the corresponding precursor. b) Derived from the gas-phase stability of the carbocation at 300 K. c) ρ value in log-scale. Multiplying the ρ of gas-phase stability by the factor of 1000/2.303RT. d) Ref. 2, in AcOH; LArSR ρ value corrected to 25 °C. e) In AcOH at 115 °C; Ref. 3. f) Ref. 30. g) In 90% aq acetone at 25 °C. Ref. 20. h) Ref. 25. i) Ref. 21. In 80% aq acetone. ρ value corrected to 25 °C. j) Ref. 26. k) Ref. 22. In 80% aq acetone at 25 °C. l) Ref. 27. m) In 80% aq EtOH at 25 °C, Ref. 23. n) Ref. 28. o) Ref. 24. In 50% aq EtOH at 25 °C. p) Ref. 29.

aryl-participation, than through a benzylic π-interaction in the transition state.[2]

Recently, we discussed the change in the resonance demand significantly observed in the intrinsic stabilities of benzylic carbocations in the gas phase.[25–29] It should be particularly noted that the r values of the gas-phase stabilities of benzylic cations are exactly the same as those observed in the solvolysis of the corresponding precursors, despite the remarkably reduced ρ values in the solution phase. Since the gas-phase stabilities are independent of any multiplicity of the kinetic process or of any mechanistic complextity, the resonance demand observed in solvolyses should be essential of incipient carbocation intermediates. The solvolysis rate and the stability of the solvolysis intermediate in the solution phase should reflect the change in the intrinsic stability of the gas-phase cations. This provides a strong basis for our contention that the nonunity r values generally observed for a series of solvolyses are essential, but not a correlational artifact arising from nonlinearity caused by mechanistic complexities.

The change of the energy profile with the substituent can be considered to be essentially noncrossing in the vicinity of rate-determining transition state, as well as of the principal intermediate in the solvolysis process.[31] The r value for the ordinary endothermic ionization process of solvolysis does not seem to be susceptible to the movement of the transition state along the reaction coordinate relative to the intermediate, whereas the ρ value can reflect, even sensitively, the position of the transition state.

In a recent study[30] we presented convincing evidence for the existence of long-lived phenonium ions under equilibrium in the gas phase, and determined, therefrom, the intrinsic stabilities of gas-phase phenonium ions by an ion cyclotron resonance method. The phenonium ion, generated as a long-lived $C_8H_9^+$ cation from electron impact ionization of 2-phenylethyl bromides, was found to be 2.4 kcal mol^{-1} (1 cal=4.184 J) more stable than the *t*-butyl cation; similarly, the α-methyl phenonium ion (6 kcal mol^{-1}) and the α,β-dimethyl one (9 kcal mol^{-1}) more stable than the *t*-butyl cation.[32] The present α,β-dimethyl phenonium ion is even more stable than the 1-phenylethyl cation. The corresponding β-phenylalkyl open cations (without bridging) should be ca. 10 kcal mol^{-1} less stable than the *t*-butyl cation. The bridged phenonium ion should intrinsically be more stable than, and capable of competing with, the corresponding open cation as the dominant intermediate in solvolysis. More significant, we have realized an excellent LArSR correlation for the intrinsic gas-phase ionization equilibrium (3) for with an r value of 0.60, exactly the same value as that of the aryl-assisted k_Δ solvolysis.[30]



(3)

These facts provide important information concerning the real picture of the aryl-assisted transition state of the solvolysis. The identity of the r value for the aryl-assisted solvolysis and the corresponding gas-phase phenonium ion equilibrium implies that the resonance demand of the solvolysis transition state is essentially determined by the intrinsic resonance demand of the intermediate phenonium ion. Intuitively, this fact can be most reasonably rationalized as the coordinate of the k_Δ transition state being very close to the phenonium intermediate. Aryl-assisted solvolysis can be regarded as being an intramolecular nucleophilic displacement of a leaving group by a β-aryl group. The reduced r value of k_Δ solvolysis has often been likely referred to the earlier transition state, as in the intramolecular S_N2 mechanism, whereas the intermediate r value, itself, should be referred to as a characteristic constant of the incipient phenonium ion. In the solvolysis process intervening a cationic intermediate of a two-step mechanism, the r values for the close-lying transition states of the decay processes should all reflect the intrinsic resonance demand of the intermediate cation. Thus, even if an r value close to unity can be assumed for the ionization step, the r value for the subsequent decay process can never be considered to be as low as r=0. This rationale may also be applied to the β-aryl-assisted process of the multistep mechanism intervening a phenonium ion intermediate. The Johnson interpretation of a non-unity r value in solvolysis in terms of a multistep mechanism involving an appropriate blending of σ^+ and σ° relationships[18] cannot be general. Either the reverse process of the k_c ionization or the recombination process of the carbocation with various nucleophiles should all be described by a single common set of substituent constants with a fixed r value; furthermore, the ρ value for the recombination processes with any nucleophilies should also be absolutely small. Accordingly, the total substituent effects (ρ_Δ and r_Δ values) on most k_Δ solvolyses are usually constant, independent of the solvent, and also independent of the presence of an internal return.

Experimental

Material: *threo*-3-Phenyl-2-butanols were synthesized from substituted bromobenzenes or acetophenones via *cis*-3-aryl-2-butenes.[33] 2-Phenyl-2-butanols were prepared by Grignard reaction of either bromobenzenes with 2-butanone or ethyl bromide with acetophenones. Tertiary alcohols were dehydrated by refluxing with Ac_2O for 4 h to olefins which were fractionarily distilled through a spinning band fractionation column to afford essentially pure *cis*-3-phenyl-2-butenes (>98%). *cis*-Butenes were converted into *threo*-3-phenyl-2-butanols by hydroboration–oxidation. The *m*-bromo derivative was not dehydrated under the above-mentioned conditions, but gave the tertiary acetate which was dehydrated to the olefin by concd H_2SO_4–AcOH according to Brown's method.[11c] Therefore, *p*-Cl, *m*-Cl, and *p*-Br derivatives were dehydrated with concd H_2SO_4–AcOH directly from the tertiary alcohols.

Table 4. Physical Data of *threo*-2-Aryl-1-methylpropyl Brosylates

Substituent	Mp/°C	Carbon/%		Hydrogen/%		Nitrogen/%	
		Found	Calcd	Found	Calcd	Found	Calcd
4-OCH$_2$CH$_2$-3[a]	94—94.5	52.63	52.56	4.68	4.66		
p-MeO	87—88[b]	51.35	51.14	4.81	4.80		
2-Fl	112—113	61.15	64.49	4.68	4.94		
p-PhO	104—105	57.40	57.27	4.59	4.59		
p-MeS	121.5—122.5	49.24	49.16	4.56	4.61		
p-*t*-Bu	67.5—68	56.47	56.47	5.93	5.92		
3,4-Me$_2$	59.5—60.5	54.41	54.41	5.28	5.33		
3,5-Me$_2$	Oil						
4-MeO-3-Cl	104—105	47.09	47.07	5.93	5.92		
p-Me	95.2—95.7[c]	53.26	53.27	4.97	5.00		
m-Me	46.5—47.0[d]	53.24		4.94			
H	94.0—94.5[e]	51.97	52.04	4.61	4.64		
p-F	85.5—86	49.53	49.62	4.05	4.16		
4-MeS-3-Cl	103—104	45.39	45.43	4.03	4.06		
p-Cl	89—90[f]	47.46	47.60	3.96	3.99		
m-Cl	66.4—67.1[g]	47.53		3.90			
p-Br	82.0—82.8	42.82	42.88	3.59	3.60		
m-Br	67—68	42.73		3.55			
p-CN	113.6—114.1	51.79	51.79	4.01	4.09	3.61	3.55
m-CN	91.5—92.5	51.78		4.09		3.44	
m-CF$_3$	49.2—50[h]	46.74	46.70	3.72	3.69		

a) See footnote c in Table 1. b) Lit,[12b] mp 97.5—98.5 °C. c) Lit,[11c] mp 97—98 °C. d) Lit,[11c] mp 47.5—48.5 °C. e) Lit,[11c] mp 94—95 °C. f) Lit,[11c] mp 68.5—69.5 °C. g) Lit,[11c] mp 91.5—92.5 °C. h) Lit,[11c] mp 50—51 °C.

Cyano-substituted butanols were prepared by a reaction of the corresponding bromo derivatives with CuCN in DMF by the Friedman–Shechter method.[34]

2-Aryl-1-methylpropyl brosylates were prepared according to the Tipson procedure[35] and recrystallized from appropriate solvents. The physical constants of the esters are listed in Table 4.

Solvent:[36] Commercial glacial acetic acid was purified by refluxing for 5 h over KMnO$_4$. The distillate was refluxed with an equivalent amount of acetic anhydride to the content of water in the presence of a trace of sulfuric acid, and then distilled through a 30 cm glass helix-packed column (bp 118—118.5 °C). The distillate was purified by redistillation through a 90 cm glass helix-packed, vacuum-jacketed still. The purity was estimated to be >99.9% from a freezing-point test.

Ethanol (95%) was dehydrated twice under reflux with magnesium ethoxide and distilled. Deionized water was refluxed with KMnO$_4$; the distillate was redistilled immediately before use. 80% aqueous ethanol (80EtOH) was prepared by mixing corresponding volumes of ethanol (80) and water (20) at 25 °C.

Kinetic Measurements: The acetolysis rates were titrimetrically determined by the usual ampoule technique and a batch technique for several reactive substrates.[36] All kinetic runs were followed over 80% completion. The solvolysis rates in 80EtOH were measured conductimetrically, as previously described.[36b] Conductance measurements were made in a cell with platinum electrodes and readings were taken with a TOA-Electronics Ltd. Conductivity Meter Model CM-50AT or CM-60S equipped with a time-interval unit and a digital printer. At a low initial concentration of the substrates (ca. 10^{-4} mol dm^{-3}) in this study, the conductance data were fitted directly to a first-order rate equation by means of a least-squares method; the precision of the fit to first-order kinetics was satisfactory (R>0.99998) over 2.5 half-lives for all runs.

Several acetolysis runs for relatively reactive or less soluble substrates were carried out conductimetrically; however, the acquired rate data might be relatively less accurate because of the relatively small change in the conductivity in acetic acid.[37]

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$$SS = \sum W(k_t(\text{obsd}) - k_t(\text{calcd}))^2$$

where $W(=1/(k_t(\text{obsd}))^2)$ was the weight of rate data.

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