Substituent Effects. XVI.[1] Acetolysis of 2-Phenylethyl Tosylates[2]

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The acetolysis rates of 2-arylethyl tosylates were determined for a series of aryl substituents. The nonlinear substituent effect was reasonably accounted for on the basis of two linear LArSR relationships; one for the aryl-assisted (Fk_Δ) and one for the unassisted (k_s) processes, respectively. A precise dissection of the apparent substituent effect into individual effects for both processes was achieved in this manner. The substituent effect on the k_s process can be described as a linear function of σ° with a small ρ_s of -0.19, and that on the Fk_Δ process in terms of the LArSR Eq., with a $\rho_\Delta=-3.87$ and an $r_\Delta=0.631$. The use of σ^+ for the Fk_Δ process failed to give any reasonable dissection. The r value for this Fk_Δ process is essentially identical to that for the neophyl solvolysis. The unique r value of 0.6 is concluded to be characteristic of β-aryl-assisted ionization processes in general.

Anchimeric assistance in solvolyses has been the subject of a number of investigations.[3] The importance of neighboring phenyl participation can be estimated from the effects of aryl substituents, which have therefore been an important tool for analyzing the exact mechanism.[2–5] Solvolysis of neophyl brosylates (2-methyl-2-phenylpropyl *p*-bromobenzenesulfonates) has often been used as a reference set for the substituent effects on aryl-assisted solvolyses,[4b,6,7] and we have recently reported[8] that the substituent effect on the neophyl acetolysis can be described by a unique r value of 0.56 in our LArSR Eq.[9]

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

This appreciably exalted r value was taken as evidence for a direct π-delocalization interaction between the aryl π-system and the β-carbocation center, i.e., a bridged structure, in the rate-determining transition state.[9,10] The most important conclusion from general LArSR analysis is that the r value can be a unique parameter characteristic of the structure of the transition state.[9] While the r parameter is a sensitive measure of the resonance demands of varying systems, it usually shows little or no variation within a family of essentially the same mechanism. It is therefore expected that the substituent effect for β-aryl-assisted solvolyses can be characterized by such a unique r value, in contrast to the traditional σ^+ characterization.[5] Accordingly, this investigation was undertaken in an attempt to define more precisely the substituent effect for the anchimerically assisted processes of 2-arylalkyl solvolysis systems.

In the acetolysis of 2-arylethyl tosylates chosen for the present study as well as in most such 2-arylalkyl solvolyses, the precise analysis of substituent effects on the rate suffers from the mechanistic complexity caused by the concurring solvent-assisted process.[2–5] The observed solvolysis rate k_t corresponds to a sum of rates, k_s+Fk_Δ, of two competing processes, aryl-assisted (Fk_Δ) and unassisted (k_s) ones. A useful way for the direct analysis of the two substituent effects has been exploited by Schleyer et al.,[4] on the basis of the assumption of a Hammett-type substituent effect correlation for the respective processes. Although this treatment achieved reasonable dissection into k_s and Fk_Δ processes, their data set involving only a few strongly activating substituents is insufficient to define precisely the substituent effect for the anchimerically assisted process. In the present study, we have extended the range of substituents of 2-arylethyl tosylates and analyzed the respective substituent effects on the k_s and Fk_Δ processes, in terms of the LArSR Eq. 1.

Results and Discussion

Rate constants of acetolysis of 2-arylethyl tosylates were determined at 115.00 °C in glacial acetic acid with initial concentrations (0.02 mol dm^{-3}) of tosylates. All runs gave good first order kinetics over more than two half-lives. The rate constants were reproducible to better than ±1% for repeated runs in a single batch of solvent, while they differed sometimes by 5—10% in different solvent batches; thus, the rate data were normalized each time to the rate of a reference substrate. The results are summarized in Table 1. As Schleyer's k_t values were found to be consistently lower than the present data by a factor of 10%, the k_t values for *m*-F, *m*-CF_3, *p*-CF_3, and 3,5-$(CF_3)_2$ derivatives calibrated by this factor were included in the present analysis.

Logarithms of relative rates are plotted against σ° and σ^+ in Fig. 1. The nonlinear behavior of the substituent effect with either set of substituent constants was pointed out earlier for this acetolysis,[3] and was accounted for by varying competition of the two non-crossover processes with the change of aryl

Table 1. Acetolysis Rate Constants of 2-Phenylethyl Tosylates

Substituents	Temp/°C	$10^5\,k_t$/s^{-1}	
		Present study	Lit. values[a)]
4-OCH$_2$CH$_2$-3[b)]	75.00	2.79 ±0.04	
	90.00	13.1 ±0.2	
	100.00	35.3 ±0.4	
	115.00	137[c,d)]	
4-MeO-3-Me	75.00	1.96 ±0.03	
	90.00	9.12 ±0.15	
	100.00	23.4 ±0.3	
	115.00	89.3[c,e)]	
p-MeO	75.00	0.867±0.001	
	90.00	4.258±0.042	
	100.08	11.22 ±0.08	
	115.00	43.4 ±0.4[f)]	40.0
3,4,5-Me$_3$	115.00	10.26 ±0.03	
p-C$_6$H$_5$O	115.00	6.86 ±0.07	6.10
2-Fluorenyl	115.00	6.82 ±0.04	7.00
3,4-Me$_2$	115.00	6.37 ±0.02	
p-MeS	115.00	5.43 ±0.02	
p-Me	115.00	3.892±0.002	
p-*t*-Bu	115.00	3.56 ±0.006	
4-MeO-3-Cl	115.00	3.275±0.006	
3,5-Me$_2$	115.00	2.322±0.008	
p-C$_6$H$_5$	115.00	1.903±0.005	
m-Me	115.00	1.68 ±0.01	1.62
H	115.00	1.309±0.001	1.27
4-MeS-3-Cl	115.00	1.196±0.005	
p-F	115.00	1.186±0.005	
4-MeO-3-CN	115.00	1.155±0.005	
p-Cl	115.00	0.931±0.002	0.845
p-Br	115.00	0.893±0.003	
4-MeS-3-CN	115.00	0.845±0.003	
m-F	115.00		0.761
m-Cl	115.00	0.790±0.001	0.728
p-CF$_3$	115.00		0.699
m-CF$_3$	115.00		0.689
p-NO$_2$	115.00	0.705±0.002	0.635
3,5-(CF$_3$)$_2$	115.00		0.584

a) Reference 4. b) 2-(2,3-Dihydrobenzofuran-5-yl)ethyl tosylate. c) Extrapolated from the rate constants at other temperatures. d) $\Delta H^{\ast}=106.3$ kJ mol^{-1}, $\Delta S^{\ast}=-28.0$ J K^{-1} mol^{-1}. e) $\Delta H^{\ast}=104.0$ kJ mol^{-1}, $\Delta S^{\ast}=-37.6$ J K^{-1} mol^{-1}. f) $\Delta H^{\ast}=106.6$ kJ mol^{-1}, $\Delta S^{\ast}=-36.7$ J K^{-1} mol^{-1}.

substituent.[3)] When the substituents are sufficiently deactivating, no participation by aryl is observed, and the compounds react exclusively by the unassisted (k_s) process. On the other hand, sufficiently electron-releasing substituents facilitate participation and such compounds react predominantly by the aryl-assisted (Fk_Δ) process.

The substituent effect on k_t ($=Fk_\Delta+k_s$) is given by

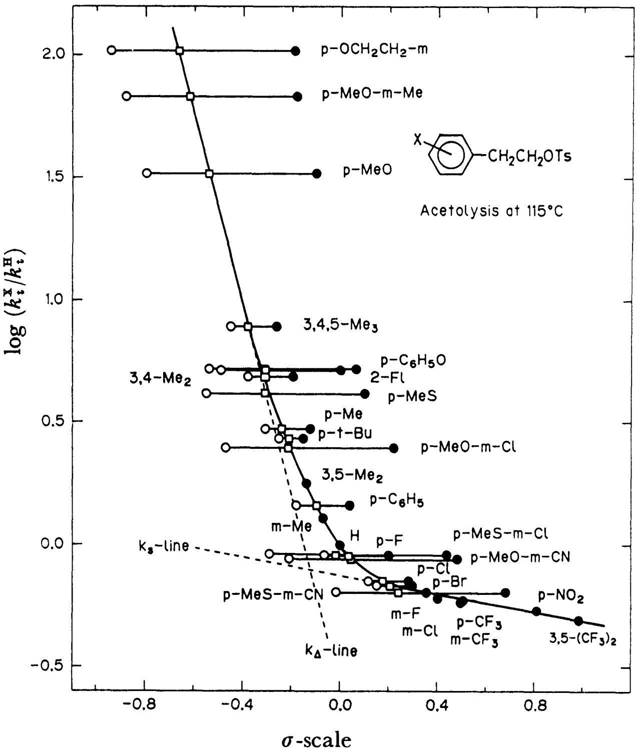

Fig. 1. Plots of log (k_t^X/k_t^H) against σ^+ (open circles), σ° (closed circles), and $\bar{\sigma}$ for $r=0.63$ (squares).

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

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 referred to $\log (k_s^H/k_t^H)$ and $\log (Fk_\Delta^H/k_t^H)$, respectively. When the second terms on the right hand side are neglected, simple Hammett-type relations 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,

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

and

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

The substituent effect on the k_s process may be treated simply with σ°, since the process involves no direct π-interaction between the aryl group and the reaction center. This permits the evaluation of the Fk_Δ values as the residues k_t-k_s for respective substituents and then the Fk_Δ substituent effect may be analyzed in terms of an appropriate $\bar{\sigma}_\Delta$. This is essentially the basis of Schleyer's treatment.[4)] The aryl-assisted process is thought to involve a significant direct π-interaction between the aryl and reaction center, and the substituent effect should be described by a set of substituent constants of the σ^+ type. Thus, Schleyer employed σ^+ as an appropriate $\bar{\sigma}_\Delta$ in his original analysis[4a] but later reported an appreciably improved result by use of the $\bar{\sigma}_\Delta$ from neophyl acetolysis.[4b] Such an appropriate $\bar{\sigma}_\Delta$ set would be described reasonably by the LArSR Eq. 1. Our analysis has therefore been carried out based on the explicit assumption that the LArSR Eq. 1 applies to both the k_Δ and k_s processes of this solvolysis. The best-fit Fk_Δ correlation was given by $\rho_\Delta=-3.87$ and $r_\Delta=0.631$, and the k_s correlation, $\rho_s=-0.186$ with σ° (r=0.00).[11] The combined correlation reproduces the $\log(k_t^X/k_t^H)$ values with excellent precision (SD=±0.027), and the fit is distinctly better than the dissection based on σ^+ as the reference $\bar{\sigma}_\Delta$ (SD=±0.10). While a precise LArSR analysis has been achieved statistically,[11] direct graphical analysis in terms of the LArSR Eq. 1 appears to be important in order to verify the LArSR analysis and to understand the nature of the Fk_Δ substituent effects.

Figure 1 is the ordinary LArSR plot for the present system. The line segments between σ^+ and σ° for the para π-donors represent resonance capabilities, i.e., $\Delta\bar{\sigma}_R^+$ values, of the respective substituents. The LArSR correlation should in general be represented by a single straight line for all substituents, and especially for para π-donors, the line divides all resonance segments at a constant internal ratio corresponding to the r value. For the present system, however, no single straight line correlation was obtained. The nonlinear correlation is of course inevitable because of the mechanistic complexity as described above.

The key principle of this graphical analysis is that only with appropriate $\bar{\sigma}_s$ and $\bar{\sigma}_\Delta$ sets, will the apparent k_t plot result in a single monotonic curvature converging to the theoretical correlation lines at either the activating or deactivating end. All meta substituents as well as para π-acceptors can unequivocally define the k_t correlation, even if nonlinear, in terms of standard σ° constants, since they are not susceptible to resonance demands (i.e., $\bar{\sigma}_\Delta=\bar{\sigma}_s=\sigma^\circ$). Such a correlation curve (solid line) ranging from 3,5-Me_2 to 3,5-$(CF_3)_2$ in Fig. 1 should be a rigid reference for analyzing the behavior of the para π-donor substituents susceptible to resonance demands. Clearly the k_t correlation curve can be extrapolated almost linearly toward the activating substrates so as to intersect the resonance segments all at a single point giving a constant ratio of 2:3. This unique ratio refers to the r value of the $\bar{\sigma}_\Delta$ set. Although the plots (squares) in Fig. 1 are shown against the statistically best-fit $\bar{\sigma}_\Delta$ set of r=0.63, there is essentially no difficulty in defining such an intersecting correlation line for p-π-donors even without the aid of the known r value. 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 accurately define the converging Fk_Δ correlation line with a ρ_Δ value of -3.87. The k_s correlation line can also be defined as the tangent line for the k_t curve at the deactivating end, giving a ρ_s value of -0.19. Both correlation (dotted) lines cross at 0.30 log-units below the k_t curve, as required for $k_s=Fk_\Delta=k_t/2$. While the k_t curve intersects the line segments of π-donors at points in between their $\bar{\sigma}_\Delta$ and σ° values in the crossover section, this is just what is expected for the effective contribution from concurrent k_s process of σ°-dependence.

On the other hand, neither the σ° nor the σ^+ plot gives any reasonable single Fk_Δ correlation line connecting smoothly to the k_t-curve. The σ^+ plot splits into three separate curves one each for strong para π-donors, weak ones (alkyl and halogen groups), and resonance-invariant substituents. The σ^+ and LArSR $\bar{\sigma}_\Delta$ correlations are contrasted most sharply by the behavior of the less activating strong π-donors, especially, m-substituted p-MeO and p-MeS derivatives.[12] These disubstituted derivatives have been shown to satisfy the LArSR relationship as united substituents having net $\Delta\bar{\sigma}_R^+$ values comparable to their parent para π-donors.[12] A series of p-π-donors with the same $\Delta\bar{\sigma}_R^+$ should provide a linear plot against σ^+ value with a slope identical to the true ρ value, regardless of the r of the system, since the $r\Delta\bar{\sigma}_R^+$ term in Eq. 1 remains constant for these groups. In fact, the σ^+ plots of strong π-donors with $\Delta\bar{\sigma}_R^+=-0.6$—$-0.7$ fall on a single line slightly curved at the bottom, covering a reactivity of over 10^2, with an identical slope to the LArSR ρ_Δ value. Similarly, the weak π-donors with $\Delta\bar{\sigma}_R^+$ of -0.15—-0.2 fall on another line with nearly the same slope, lying rather close to reference k_t curve. Note that neither line collapses into the reference k_t correlation curve, and the gap between the lines which should correspond to the $(1-r)\Delta\bar{\sigma}_R^+$ term in LArSR Eq. can be eliminated to coalesce to a single line, by use of $\bar{\sigma}_\Delta$ with an appropriate r value. While there is controversy concerning the real merit of r parameter,[13] 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.

The above LArSR results are all consistent with the presently accepted mechanism. The complete dissection attained with the k_t substituent effect provides strong support for the accepted competition mechanism, consisting of a non-crossover k_s and a k_Δ processes. The small ρ_s value for the k_s process may be attributed primarily to the relatively long distance between the substituents and the reaction center, as well as the intrinsic S_N2 character of the transition state involving less effective charge separation. The exalted r_Δ value for the assisted process provides evidence for a direct π-delocalization interaction between the aryl π-system and the β-carbocation center in the rate-determining transition state, and further suggests that the charge delocalization in this aryl-assisted transition state should not be as effective as the benzylic π-delocalization in the 1-methyl-1-phenylethyl solvolysis. The large ρ_Δ value compared with those for the ordinary unassisted β-solvolyses[3] of structurally equivalent systems is also in line with the bridged transition state.

Finally, it should be emphasized that the ρ_Δ and r_Δ values for the present Fk_Δ process are nearly identical with those for the neophyl solvolysis.[8] Furthermore, similar ρ_Δ and r_Δ values have also been obtained for other aryl-assisted processes. It therefore appears likely that the substituent effect for the β-aryl-assisted process can be characterized by this unique r value. An important criticism against our LArSR concept is that the deviation of r from unity or zero may be caused by the mechanistic complexity of the system.[13] The aryl-assisted process of 2-phenylethyl tosylates is indeed a complex one involving significant internal return.[14] On the other hand, neophyl brosylate is thought to solvolyze via a rate-determining aryl-assisted transition state uncomplicated by either internal return or nucleophilic solvent assistance. The essential identity of r_Δ values for both β-aryl-assisted processes indicates that the r value should be determined only by the common rate-determining step, aryl-assisted ionization without return. This fact strongly argues against the interpretation of an intermediate r value in terms of the mechanistic complexity of the reaction.[2,8] As a conclusion, the r value of 0.6 must be characteristic of aryl-assisted ionization process, and the resonance demand of the Fk_Δ process differs intrinsically from the demand r=1.00 defined by the 1-methyl-1-phenylethyl solvolysis. Further discussion will require comparative studies on related systems which involve varying degrees of mechanistic complexity, and also a detailed examination of the results of the statistical analysis.

Experimental

Material. Most of the phenylacetic acids were prepared by the Willgerodt reaction of the appropriate acetophenones. 2-Phenylethyl alcohols were obtained by $LiAlH_4$ reduction of the corresponding acids or esters, as described previously.[2]

2-(3-Cyano-4-methoxyphenyl)ethanol was prepared from *p*-methoxyphenylacetic acid. Bromination of *p*-methoxyphenylacetic acid with Br_2 in acetic acid at 40—45 °C gave 4-MeO-3-Br-phenylacetic acid, mp 116—117 °C, recrystallized from ethanol-water. 4-MeO-3-Br-phenylacetic acid was treated with $LiAlH_4$ and immediately decomposed, since prolonged reaction caused a considerable loss of the bromo group. The crude alcohol, bp 149—151 °C/3 mmHg (1 mmHg=133.322 Pa), containing 5% 2-(*p*-methoxyphenyl)ethanol, was treated with CuCN in DMF and decomposed with $FeCl_3$–HCl, according to the Friedman and Shechter procedure,[15] to give 2-(4-MeO-3-CN-phenyl)ethanol, bp 179—180 °C/3 mmHg, after purification through SiO_2 column.

2-(3-Cyano-4-methylthiophenyl)ethanol was prepared in a similar way as the *p*-MeO derivative. Quick bromination with 2 equiv bromine at 45 °C gave crude acid contaminated with methylsulfoxide derivative which was purified by SiO_2 chromatography, mp 102—103 °C. 2-(4-MeS-3-Br-phenyl)-ethanol and 3-cyano-4-methylthio derivative were purified by chromatography, mp 58—59 °C and mp 40—41 °C.

2-(*p*-Bromophenyl)ethanol was prepared in the usual manner from *p*-bromoacetophenone, via methyl phenylacetate (bp 89—90 °C/0.25 mmHg); bp 103—104.5 °C/2.5 mmHg.

2-(Substituted phenyl)ethyl *p*-toluenesulfonates were synthesized from the corresponding alcohols and tosyl chloride by the Tipson procedure[16] and purified by recrystallization from appropriate solvents. Physical constants of most esters were reported in a previous paper,[2] or are described below.

2-(3-Cyano-4-methoxyphenyl)ethyl tosylate, mp 109.7—110.5 °C. Found: C, 61.57; H, 5.26; N, 4.31%. Calcd for $C_{17}H_{17}NO_4S$: C, 61.61; H, 5.17; N, 4.23%. 4-MeS-3-CN derivative, mp 77—77.5 °C. Found: C, 58.87; H, 4.72; N, 4.19%. Calcd for $C_{17}H_{17}NO_3S_2$: C, 58.77; H, 4.93; N, 4.02%. *p*-Br derivative, mp 91 °C. Found: C, 50.92; H, 4.34%. Calcd for $C_{15}H_{15}O_3SBr$: C, 50.71; H, 4.26%.

Kinetic Measurement. The acetolysis rates were measured by the titrimetric method using the usual ampoule technique. Ten cm^3 (0.02 mol dm^{-3}) aliquots were pipetted into 25 cm^3 of cold acetic acid containing sodium acetate (0.0088 mol dm^{-3}) and titrated with perchloric acid (ca. 0.025 mol dm^{-3}) in acetic acid. The mixture of crystal violet and α-naphtholbenzein was used as indicator.

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11) Both the iterative least-squares method used by Schleyer[4] and nonlinear least-squares method (Newton method) were applied to the analysis. Identical result was obtained by assuming fixed r_s value at 0, 0.27 for reducing a variable. Use of $\bar{\sigma}_\Delta$ from neophyl solvolysis ($r_\Delta=0.58$ a fixed) gave closely the same correlation; $\rho_\Delta=-4.04$, $\rho_s=-0.16$ ($r_s=0$) with a good precision (SD=±0.036). Use of σ^+ for $\bar{\sigma}_\Delta$ ($r_\Delta=1.00$ a fixed) gave a correlation; $\rho_\Delta=-3.55$, $\rho_s=-0.58$ ($r_s=0$) with a lower precision (SD=±0.10); unreasonable ρ_s value and the position (k_s^H) may be noticed.

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