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SUBSTITUENT EFFECTS IN THE SOLVOLYSIS OF BENZYL TOSYLATES

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The substituent effect on the rates of solvolysis of substituted benzyl tosylates in acetic acid was analysed based on the Yukawa–Tsuno LArSR equation. Neither the LArSR nor simple σ^+ treatment was capable of providing any linear correlation plot for the full range of substituents. The σ^+ plot was not simply bilinear but widely scattered, giving a split pattern of parallel curves with significant gaps. Since any mechanistic transition with substituents should bring about a single continuous curve when plotted against an appropriate substituent constant scale, the split σ^+ plot is not in line with an interpretation in terms of a mechanistic transition. On the other hand, the LArSR plots with $r = 1{\cdot}3$ coalesced into a single smooth curve including the *meta* correlation curve. A different resonance demand as high as $r = 1{\cdot}3$ is required in order to give a smooth single-curve correlation for the entire substituent range without splitting. For the reactive substituents down to *p*-halogens, a sufficiently linear plot can be obtained against a set of substituent constants with $r = 1{\cdot}3$ which can be referred to the substituent effect correlation for the k_c mechanism of this system. An identical *r* value was likewise assigned for the k_c mechanism of the hydrolysis for a more severely restricted range of activating substituents down to the 4-MeS-3-CN group.

INTRODUCTION

Recently we have reported a detailed analysis of the substituent effect on the solvolysis of benzyl tosylates in aqueous acetone,[1] on the basis of the equation[2]

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

The resonance demand (*r*) of this solvolysis has been concluded to be significantly higher than unity defined for the solvolysis of *tert*-cumyl (1-methyl-1-phenylethyl) chlorides. An *r* values as high as $1{\cdot}30$ leads us to conclude that the benzyl k_c substituent effect must be far beyond the scope of the simple Brown $\sigma^+\rho^+$ treatment:

$$\log(k/k_0) = \rho^+\sigma^+ \qquad (2)$$

The analysis of the substituent effect on the solvolysis of benzyl tosylates so far suffers from the non-linear behaviour[3–6] due to a k_c–k_s mechanistic transition. For the bisected σ^+ correlation with different ρ^+ values each for activating and deactivating ranges of substituents, there has been general agreement of opinion about the interpretation of the curve break in terms of a mechanistic change from a k_c mechanism for the former range to a k_s mechanism for the latter range of substituents.[3b,4a,5,6] The benzyl solvolysis is not completely limiting in the relatively less nucleophilic acetic acid[5] and in 97% aqueous trifluoroethanol (TFE)[6,7] and even for solvolysis in 97% hexafluoroisopropanol, a solvent of high ionizing power and low nucleophilicity, a curve break in the σ^+ plot was reported.[6]

Whereas in all these previous studies the Brown σ^+ was utilized as a suitable reference scale for describing the substituent effect in this system, all the arguments are based simply on the fact that the curved plot is not straightened even by application of the Brown σ^+ constant. Recently, we have shown that the k_c process of this solvolysis in 80% aqueous acetone solution has an *r* value clearly higher than unity for the *tert*-cumyl solvolysis.[1] The mechanistic transition with a substituent is clearly evident in this solvolysis in most solvents, and there is no reason to assume a single linear substituent effect for the entire range of substituents. Since the solvent used in this study, acetic acid, differs considerably in nucleophilicity rather than in the ionizing power from 80% aqueous acetone, the same k_c mechanism controlled by the ionizing power of solvents can be expected for both acetolysis and hydrolysis, at least as far as the k_c regions are concerned. The solvent nucleophilicity will be reflected in the k_s mechansim in the electron-withdrawing region.

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As nucleophilic solvent participation may become important for electronegative derivatives, the effect of nucleophilicity will be more significant in hydrolysis rather than in acetolysis and will be less significant even for a more electron-attracting derivative in acetolysis. The effects of sufficiently activating substituents in acetolysis should be free from the non-linearity due to a mechanistic shift. Previous studies[3–6] were based on only a few typical substituents and involved no key substituents for estimating the r value of the k_c process of this system. Accordingly, we have determined the rate data for some important substituents, especially strong *para* π-donors, and the effects are analysed based on our LArSR equation (1) in comparison with the Brown σ^+ treatment.

Table 1. Acetolysis of benzyl tosylates

Substituent	Temperature (°C)	10^5k (s^{-1})
p-PhO	25·0	1350[a]
4-MeO-3-Cl	25·0	773,[b] 898[a]
2-F	25·0	555[a]
4-MeS-3-Cl	25·0	87·0, 96·5[a]
4-MeS-3-Br	25·0	100[a]
3,4,5-Me_3	25·0	111, 115[a]
3,4-Me_2	25·0	43·9, 48·5[a]
4-MeO-3-CN	25·0	21·8, 21·1[a]
p-Me	25·0	17·7, 19·6,[a] 21·8[b]
p-*i*-Pr	25·0	13·3, 16·7[a]
p-*t*-Bu	25·0	8·06, 11·7[a]
p-Ph	25·0	6·95, 9·76[a]
2-Naph	25·0	4·80[a]
4-MeS-3-CN	25·0	2·656, 2·36[a]
3,5-Me_2	25·0	1·26, 1·24[a]
p-F	25·0	0·813, 0·712,[c] 0·75[a,c]
m-Me	25·0	0·577, 0·872[b]
H	25·0	0·269, 0·315,[b,d] 0·279,[c] 0·261[e]
p-Cl	25·0	0·135[c]
p-Br	25·0	0·0990
m-Cl	25·0	0·0136,[c] 0·0162[b,f]
m-CF^3	45·0	0·0796[c,f]
	25·0	0·0069[c,f]
p-CF_3	25·0	0·0045[c,f]
p-NO_2	25·0	0·00200[d,g]
	75·0	0·480
	115·0	13·92
3,5-$(CF_3)_2$	25·0	0·00118[d,h]
	75·0	0·289
	115·0	8·50

[a] Conductimetric (see Experimental).
[b] Ref. 4b.
[c] Ref. 5.
[d] Calculated from rate data at other temperatures.
[e] Containing 0·2 wt-% of acetic anhydride at 25·05 °C.[8a]
[f] Extrapolated from other temperatures based on literature values.
[g] $\Delta H^{\neq} = 92{\cdot}1{\cdot}0\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq} = -83{\cdot}4\ \mathrm{J\,K^{-1}\,mol^{-1}}$.
[h] $\Delta H^{\neq} = 92{\cdot}5\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq} = -86{\cdot}5\ \mathrm{J\,K^{-1}\,mol^{-1}}$.

RESULTS AND DISCUSSION

The rates of acetolysis of a series of benzyl tosylates were determined by titrimetric and conductimetric methods in glacial acetic acid, and the kinetic data are summarized in Table 1, together with the relevant literature data.

Figure 1 shows the relationship for logarithmic rates between solvolysis in acetic acid and 80% aqueous acetone. There is no simple linear free energy relationship but a bilinear one for whole substituent range. The activating substrates ranging from a *p*-phenoxy to a β-naphthyl group give a good partial linear relationship with a slope of unity over a 10^3 change in reactivity and the deactivating substrates give another partially linear relationship with a significantly reduced slope.

Figure 2 shows the substituent effect on benzyl solvolysis in acetic acid. The σ^+ plot does not provide a simple bilinear pattern but a significantly split pattern with apparently parallel curvatures with significant gaps for strong π-donors, for weak π-donors such as alkyl groups and for non-conjugative *meta* substituents including p–π acceptor substituents. The dispersion behaviour of the σ^+ correlation is similar to that observed for solvolysis in aqueous acetone.

As mentioned before, the solvolysis mechanism changes with substituents from the k_c mechanism for the activated region of substrates to the k_s mechanism for the deactivated region of substrates. The substrates reacting by either the k_c or k_s mechanism should satisfy a linear substituent effect relationship characteristic of their own mechanism. Either correlation can be related linearly with an appropriate substituent constant scale, i.e. the scale with an appropriate r value in the LArSR equation (1). The ρ value should differ significantly for

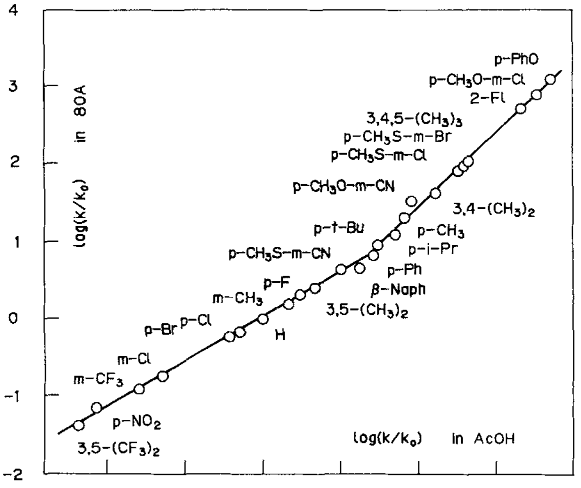

Figure 1. Logarithmic rate plots of the solvolysis of benzyl tosylates in 80% aqueous acetone vs those in acetic acid

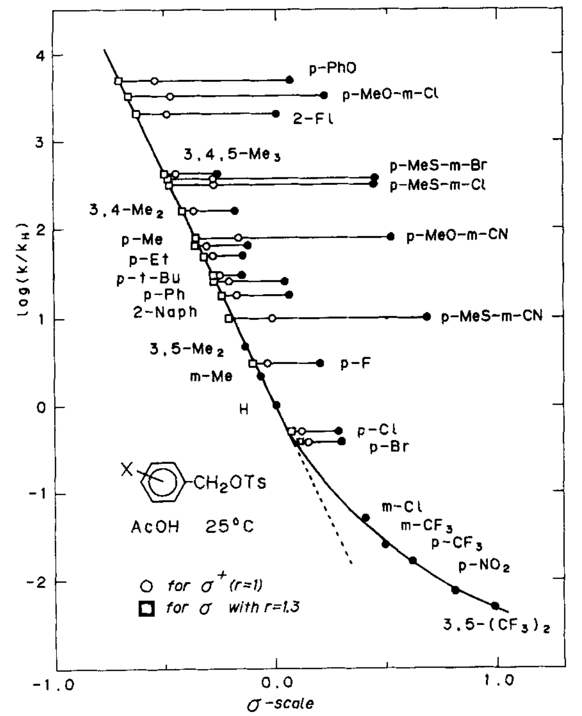

Figure 2. LArSR plots of acetolysis of benzyl tosylates: ○, σ^+; ●, σ^0; □, $\bar{\sigma}$ for $r = 1\cdot3$

activated and deactivated substituent regions, reflecting different mechanisms or different charge developments in the transition states. As the mechanistic transition itself should be a continuous function of substituent polarities, any mechanistic change should give rise to a single smooth-curved or a bisected correlation for the whole range of substituents when plotted against an appropriate set of substituent constants. Hence the simple bilinear correlation between the hydrolysis and acetolysis rates in Figure 1 is consistent with this interpretation in terms of mechanistic transition. Since both solvents differ widely in nucleophilicity but not in ionizing power, the linear relationship with a slope of essentially unity for the activated region of substituents may argue for a predominantly k_c mechanism for acetolysis and hydrolysis. The ρ value remains the same for the k_c region in both solvents. On the other hand, the solvent nucleophilicity is reflected in the different ρ values for the k_s mechanism occurring in the deactivated region. It should be noted that a common substituent constant scale can be applied to describe the substituent effects of this reaction in both solvents. On the other hand, the significantly split nature of the σ^+ plot in Figure 2 conflicts with the interpolation in terms of a mechanistic change and suggests the inadequacy of σ^+ scale for this reaction.

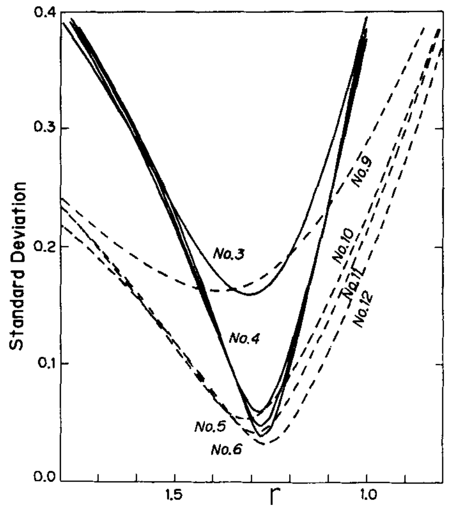

Figure 3. Plot of standard deviations as a function of r for the solvolysis of benzyl tosylates in acetic acid. The numbers refer to the set numbers in Table 2

In Figure 2, the plots for r-independent substituents (*meta* substituents and p$-\pi$ acceptor substituents) fall on a single smooth curve, which defines unequivocally the ρ correlation line, even if non-linear, in terms of a definite substituent constant scale. The non-linear ρ_m correlation line represents the correlation of actual substituent effect reflecting precisely the mechanistic shift, and may be a rigid reference of the correlation analysis. The plot of *para* π-donors against an appropriate $\bar{\sigma}$ scale should all coalesce into a single smooth curve, including the *meta* correlation curve. The line segments between σ^+ and σ^0 for p$-\pi$ donors in Figure 2 represent their $\Delta\bar{\sigma}_R^+$ values. The LArSR correlation can be given by a straight line dividing all the resonance segments at a constant external ratio corresponding to the r value. A high resonance demand of $r = 1\cdot3$ is required in order to give a smooth single-curve correlation for the entire substituent range without splitting. This simple graphical interpretation is confirmed quantitatively by the results of correlation analysis. Sufficient linearity can be observed for the reactive range of substituents down to the *p*-chloro group, over 10^4 reactivity, against a set of substituent constants with $r = 1\cdot3$. This r scale can be referred to the substituent effect correlation of the k_c mechanism of this system. In a previous study of the hydrolysis of benzyl tosylates,[1] the same r value for the k_c mechanism was obtained only for the more restricted range of substituents down to the 4-MeS-3-CN group.

The results of the LArSR analysis for varying ranges of substituents are summarized in Table 2. The overall correlation (set No. 1) for all substituents is of course

Table 2. Results of correlation analysis in solvolysis of benzyl tosylates in acetic acid at 25 °C

No.	Substituent sets	Correlation	n[a]	ρ	r	SD[b]	R[c]
1	All	LArSR	25	−3·444	1·524	0·401	0·9765
		σ^+	25	−4·113		0·572	0·9492
2	$\geqslant p$-CF$_3$[d]	LArSR	23	−4·406	1·337	0·207	0·9922
		σ^+	23	−5·132		0·405	0·9681
3	$\geqslant m$-Cl[e]	LArSR	21	−4·803	1·304	0·163	0·9935
		σ^+	21	−5·562		0·395	0·9589
4	$\geqslant p$-Halogens[f]	LArSR	20	−5·230	1·279	0·062	0·9989
		σ^+	20	−5·987		0·377	0·9548
5	$\geqslant p$-Cl[g]	LArSR	19	−5·323	1·274	0·049	0·9992
		σ^+	19	−6·091		0·386	0·9474
6	$\geqslant$ H[h]	LArSR	18	−5·408	1·269	0·039	0·9994
		σ^+	18	−6·194		0·396	0·9368
7	$\geqslant m$-Me[i]	LArSR	17	−5·444	1·270	0·036	0·9995
		σ^+	17	−6·036		0·403	0·9257
8	Excluding disubstituted	LArSR	20	−3·126	1·947	0·386	0·9788
	strong 5-donors[j]	σ^+	20	−3·876		0·534	0·9566
9	$\geqslant m$-Cl[e] of No. 8	LArSR	16	−4·580	1·388	0·168	0·9936
		σ^+	16	−5·345		0·286	0·9798
10	$\geqslant p$-Halogen[f] of No. 8	LArSR	15	−5·100	1·312	0·056	0·9992
		σ^+	15	−5·879		0·223	0·9853
11	$\geqslant p$-Cl[g] of No. 8	LArSR	14	−5·226	1·289	0·044	0·9994
		σ^+	14	−6·114		0·209	0·9859
12	$\geqslant$ H[h] of No. 8	LArSR	13	−5·385	1·261	0·033	0·9996
		σ^+	13	−6·458		0·181	0·9881

[a] Number of substituents involved.
[b] Standard deviation.
[c] Correlation coefficient.
[d] More reactive substrates than p-CF$_3$ including p-CF$_3$.
[e] More reactive substrates than m-Cl including m-Cl.
[f] More reactive substrates than p-halogens including p-halogens.
[g] More reactive substrates than p-Cl including p-Cl.
[h] More reactive substrates than H including H.
[i] More reactive substrates than m-Me including m-Me.
[j] Excluding 4-MeO-3-Cl, 4-MeO-3-CN, 4-MeS-3-Br, 4-MeS-3-Cl and 4-MeS-3-CN.

poor, and the poor fit undoubtedly arises from the inclusion of substituents reacting by the k_s mechanism.

The LArSR correlation for the reaction having a ρ value of ca −5 is generally considered to involve an uncertainty of the order of 0.08 [standard deviation (SD)], which may be taken as a criterion for acceptable conformity to equation (1). Hence the LArSR correlation for the all-substituents set (No. 1) is obviously unsatisfactory with reference to this acceptance level. By deleting the points for m-halogens and more deactivating groups (set No. 4 in Table 2), the precision of the fit is improved to achieve a criterion of acceptable conformity, to arrive at a minimum SD of ca 0·06. Neither ρ nor r changes any more with further change in the substituent range. Only within a restricted range of substituents more activating than p-halogen can an acceptable LArSR correlation be achieved by an r value of 1·3. This r value for the k_c mechanism appears to be completely independent of any effect of deactivated derivatives for which the k_s mechanism would be considered, and allows the boundary of substrates reacting by the k_c mechanism to be defined.

The corresponding Brown σ^+ correlations (in Table 2) are distinctly poor by this criterion. Whereas the σ^+ correlation is considerably improved by excluding more deactivating groups than p-NO$_2$ (set No. 2), the precision does not appear to exceed an SD of 0·3, much worse than the limit of acceptable conformity, and is not improved by further limiting the range of substituents.

The interpretation in terms of a k_c–k_s mechanistic transition cannot be applied, in a strict sense, to any scattered σ^+ correlation. The basic requirement for this interpretation should be an adequate substituent effect scale to give a single continuous plot without significant splitting, namely a substituent constant scale with a resonance demand $r = 1·3$ in the LArSR equation (1).

The solvent-assisted mechanism may be reasonably assigned to the electron-withdrawing region giving a significantly reduced ρ value. The curve break is significant at the 4-MeS-3-CN derivative in nucleophilic 80% aqueous acetone, and at the *p*-halogens in less nucleophilic acetic acid. The ρ value for the electron-withdrawing portion is as low as $-0{\cdot}92$ in 80% aqueous acetone and $-1{\cdot}50$ in acetic acid, suggesting a k_s mechanism with a reduced central charge development in the transition state. In addition, the k_s contribution has been found to be not very significant even at the *m*-halogen derivative in the highly ionizing and relatively less nucleophilic 97% TFE.[7,8b] These results indicate that increased solvent participation is a mechanistic change which can cause a break in the LArSR plot of this solvolysis reaction. The solvolysis of benzyl mesylates in 97% aqueous hexafluoroisopropanol (HFIP) was reported to give a ρ^+ value of $-11{\cdot}6$ for the electron-donor portion of the σ^+ plot and $-5{\cdot}1$ for the electron-withdrawing portion.[6] The significant difference in the ρ values for both portions was attributed to a mechanistic change arising from nucleophilic solvent participation even in the relatively nonnucleophilic HFIP solvent.[6] This is not in line, however, with the linear k_c correlation with the usual ρ and r values observed for the range down to *m*-halogens in similarly less nucleophilic 97% TFE solution.[7,8b] Further, the ρ^+ value for the k_s portion in HFIP is equivalent to the ρ value for the electron-donor portion to be assigned to the k_c mechanism in nucleophilic solvents. We are doubtful about this extremely high ρ^+ for the benzyl k_c mechanism in HFIP, one of the largest values seen to date, or even higher than the ρ^+ value for the gas-phase stability of unsolvated carbocations.[9] The range of substituents on which the reported ρ^+ value[6] was based is too narrow to draw any decisive conclusion. The currently available data including our unpublished data for *p*- and *m*-halogen derivatives in 97% TFE appear to indicate neither a high ρ^+ value nor a significant break of the plot at the *p*-halogen derivatives.[7] The ρ value for whole range of substituents is not very different from that for the k_c correlation in nucleophilic solvents, and the apparent break in the σ^+ plot may be due to specific substituent–solvent interactions which are commonly observed for fluorinated solvents.[8b,10]

The involvement of the solvent is always an important cause of confusion in the interpretation of substituent effects on benzylic solvolyses. The substituent effect on the intrinsic stability of benzyl cations has become available based on the gas-phase chloride-transfer equilibrium of benzyl chlorides,[9] which is of course free from any mechanistic involvement of the solvent and will be directly related to the k_c ionization process in the solvolysis.

The substituent effect on the benzyl cation stability was found to be intrinsically non-linear with respect to that on the cumyl cation stability, suggesting a varying resonance demand with the parent cation stability.[9] The LArSR theory can be equally applicable to gas-phase substituent effects, and the intrinsic carbocation stability of the benzyl cation must have an enhanced resonance demand compared with the α,α-dimethylbenzyl cation. Most important, the r value for gas-phase benzyl cation stability has been found to be identical with that for the benzyl k_c solvolysis of activated range of substituents.[1a,9,11] The charge delocalization in the k_c transition state of solvolysis should be quite close to the delocalization within the carbocation intermediate. As a conclusion, the enhanced r value of $1{\cdot}3$ for the benzyl k_c solvolysis must represent the intrinsic resonance demand of benzyl cation. This provides a strong basis for our contention that the enhanced r value obtained for the present solvolysis is not a correlational artifact[12] arising from non-linearity caused by mechanistic complexity.

Validity of *r* value

As described in previous papers,[1,11,13] the significance of the parameter r can be examined by following the change in the standard deviation of statistical fitting to equation (1) as a function of r without constraint on the ρ value.

In Figure 3, the solid curves refer to the unrestricted substituent sets including *m,p*-disubstituted derivatives, and the dashed curves to the sets consisting of only typical substituents without disubstituted derivatives. The SD vs r curves for the all-substituents set (set No. 1 in Table 2) and set No. 2 are not shown in Fig. 3 but have no significant minimum at the best-fit r value. In the solid-line series, curve 3 of set No. 3 does not attain a sufficient depth below the SD line of acceptable conformity, indicating the inclusion of some k_s substrates in the set. Curve 4 for set No. 4 for the more reactive range than *p*-halogens gives an SD vs r curve as a sharp wedge with sufficient depth of small minimum SD. No significant change in the curve is observed even if the *p*-Cl point is deleted.

A significant difference in broadness between the solid and dashed curves can be seen. Sufficient depth of a small minimum SD should be the basic requirement for an acceptable correlation, whereas the steepness is a more direct measure of the reliability of the r value. The latter will be of particular importance for discussing the validity of the resonance demand for the k_c mechanism of this reaction. In the dashed-line series consisting only of simple *para* π-donors without disubstituted ones, set No. 9 shows a considerably improved correlation with a higher r value, but fails to give any deep minimum. Whereas the LArSR analysis may give a better correlation than the corresponding σ^+ one, the higher r value obtained for these sets should be an artifact caused by the non-linearity due to the k_c–k_s mechanistic change.[12] The minimum SD points of these sets are all still above the precision level of acceptable conformity, evidently indicating that the LArSR equation (1) fails to describe the substituent effect in these sets. In order to achieve an acceptable conformity, the LArSR equation must be applied to a more severely limited range of substituents, such as set No. 10, which must be referred to the actual range reacting by a fixed k_c mechanism of the benzyl system. The pattern of change of the SD vs. r curve with the range of substituents appears to be must more straightforward in acetolysis rather than in hydrolysis. A sufficiently deep minimum can be attained readily to overcome a level of acceptable conformity by deleting *m*-halogens and other deactivators, whereas no improvement in depth is observed by exclusion of further substituent points. There is a significant difference in broadness between the solid- and dashed-line series.

The reliability of the r value may be measured from the width of the SD vs. r plot at an SD level of 0·08 of acceptable conformity. Thus, the r value estimated for set No. 5 may be valid within an uncertainty limit of the order of 0·06, whereas for the corresponding simple π-donor set No. 11, a lower validity of the order of 0·10 is estimated. Of course, these reliability parameters could not be compared in magnitude directly with the ordinary precision indices in statistics. Nevertheless, they appear to be appropriate for the discussion of the validity of r values. Set No. 10 gives a more accurate best-fit correlation of a smaller SD value than set No. 4, but the latter gives a much steeper curve with more significant convergence than the former. Clearly, the steepness at the bottom, and hence the validity of the correlation, depend appreciably on the substituents in the set.

The statistical LArSR analysis basically requires non-linearity between σ^0 and $\Delta\bar{\sigma}_R^+$, and especially for differentiating between the LArSR and Brown σ^+ analyses the basic requirement of non-linearity between σ^+ and $\Delta\bar{\sigma}_R^+$ for π-donor substituents should be considered closely. As far as single π-donor substituents in common use are concerned, there is an intrinsic close linearity between the Brown σ^+ constants and $\Delta\bar{\sigma}_R^+$.[1a] The stronger p$-\pi$ donors are localized at the most reactive end of the σ^+ plot and tend to deviate significantly only at that end responding to the r value of the system, resulting in a concave plot indiscernible from the curvature caused by mechanistic changes. Such a curve break may become significant or serious only if the r value of the reaction is different significantly from unity, even without involving any mechanistic transition.

Many examples of non-linear σ^+ correlations have recently become available in the literature for solvolyses proceeding via highly electron-deficient benzylic carbocations.[11,14-17] For 1-trifluoromethyl-1-phenylethyl tosylates, Liu and co-workers[15] reported an extremely high ρ^+ value of -10 for the electron-donor region but -6 for the electron-acceptor region of substituents, whereas we obtained an excellent LArSR correlation with a high r value of 1·39 for the whole substituent range. It should be emphasized that the employment of the Brown σ^+ scale will be the only cause of a curve break in many such systems having significantly different resonance demands.[17] The behaviour of strong π-donor substituents with less negative σ^+ values in disturbing the σ^+ vs $\Delta\bar{\sigma}_R^+$ linearity should be most effective in distinguishing the real cause of non-linear σ^+ plots. In the present study, we utilized *m*-chloro- and *m*-cyano-substituted strong p$-\pi$ donors as such key substituents, and their importance in determining accurate r values is clearly demonstrated by the large difference in steepness between solid and dashed series of SD vs r curves.[1,11,13]

EXPERIMENTAL

Materials. The preparation of substituted benzyl tosylates was described previously.[1b] Acetic acid was purified in the standard manner as described elsewhere.[18]

Rate measurement. The rates of acetolysis were determined by the ordinary titrimetric method, using the usual ampoule technique for less reactive substituents at high temperature and the batch technique for relatively reactive substituents.[18] Acetolysis rates for reactive substituents were determined conductimetrically. Because of the relatively small change in conductivity in acetic acid,[5,19] the rate data might be relatively less accurate.

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