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RESONANCE EFFECT IN SOLVOLYSIS OF 1-METHYLBENZYL CHLORIDES

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Abstract: Substituent effects of p-MeO and p-MeS groups deactivated by additional m-substituents in cumyl and α-phenylethyl solvolyses were studied to provide evidence for the higher resonance demand in the α-phenylethyl system.

While the Brown $\rho\sigma^+$ equation has been applied as a practical means of correlating carbocation reactions,[1] our LArSR equation (1) has been shown to give more reasonable correlations generally for a variety of reactions.[2-4]

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

The r value was found to vary with reactions or the structures of transition states. We thus concluded that the r value is a parameter characteristic of a given reaction, measuring the resonance demand, the degree of resonance interaction between the aryl and reaction site in the rate-determining transition state. Although LArSR correlations have generally been interpreted in this manner,[5] a contrary view has been held based on general constancy of the σ^+ value for p-methoxy group in a series of *tert.* benzylic solvolyses.[6]

In a foregoing paper,[4a] we reported that the solvolysis of m- and p-substituted 1-methylbenzyl chlorides (PhEt-Cl) in 80% aqueous acetone gave an excellent correlation with Eq. (1), giving an enhanced r of 1.15. The higher r-value was referred to the higher resonance demand of this *sec.* system than the σ^+ reference system. However, the secondary solvolysis has been formulated as borderline case; that is, the faster solvolyzing derivatives have an even greater tendency to react by the limiting mechanism while the slower ones have a tendency toward more S_N2 like behavior of a reduced ρ value.[7] Such mechanistic transition has often been taken as a probable cause of the deviation from otherwise linear σ^+ relationship,[8] even in the present reaction negating the improved LArSR correlation. In order to rationalize the substituent effect on this system, a critical examination should be required on the effect of mechanistic transition on the r value.

If the σ^+ value with fixed resonance demand ($r = 1.00$) is appropriate for benzylic solvolyses, different substituents with identical σ^+ values, *isopolar* substituents, should give the same rate with the same mechanism. On the other hand, if the varying resonance demand is the case, any *isopolar* π-donors of different $\Delta\bar{\sigma}_R^+$ may result in different rates, responding to resonance demands. Such behavior of *isopolar* π-donor set would be utilized as a probe of distinguishing the cause of the non-linear σ^+ plot of PhEt solvolysis. In order to detect a small difference in r between systems, sets of *isopolar* substituents having significantly different $\Delta\bar{\sigma}_R^+$ values should be required. In the present study, we have chosen p-MeO and p-MeS groups deactivated by additional meta halogen or cyano group as strong π-donors pairing with appropriate reference substituents.

The rates of solvolysis of 1-arylethyl chlorides were determined in 80% aq. acetone at 45°C, and the σ^+ values were determined directly from the solvolysis of corresponding *t*-cumyl chlorides in 90% aq. acetone (Table 1). The σ^+ values of disubstituted derivatives were defined for the overall effects of the two substituents as a united substituent. Their approximately additive or even negative σ^+ values indicate no steric loss of resonance of p-substituents and suggest that the $\Delta\bar{\sigma}_R^+$ values are essentially unchanged from the parent ones. The σ^+ values in Table 1 permit grouping these substituents into three *isopolar* sets, each of which may be characterized by well-established σ^+ of 2-Fl, p-*t*-butyl, or H (or m-cyclopropyl) group. Yet the PhEt solvolysis shows appreciable change in reactivity within each *isopolar* set. All the disubstituted π-donors enhance the rate relative to the reference one by a factor of *ca.* 2, or 0.06 ~ 0.08 σ unit as $\rho \cong -5$. Thus, p-MeS-m-Cl shows even higher rate than p-Me of large σ^+. The enhancement of p-MeO-m-Cl is less significant relative to 2-Fl because of comparable $\Delta\bar{\sigma}_R^+$, while significant relative to 3,4,5-$(CH_3)_3$ of small $\Delta\bar{\sigma}_R^+$. The rate-enhancement depending on the $\Delta\bar{\sigma}_R^+$ within each *isopolar* set

Table 1. Rates of solvolyses of PhEt and cumyl chlorides

Subst.	*t*-Cumyl-Cl			α-PhEt-Cl
	$10^5k(s^{-1})^a$	$\sigma^{+\,b}$	$\Delta\bar{\sigma}_R^+$	$10^5k(s^{-1})^c$
p-MeO-m-Cl	2200	-0.490	-0.70	545
p-MeO-m-Br	2220	-0.491	-0.70	539
2-Fluorenyl	1860	-0.474	-0.49	379
3,4,5-Me_3	1260	-0.437	-0.187	139 (210)[d]
p-Me	322	-0.311	-0.187	34.0
p-MeS-m-Cl	215	-0.270	-0.7	42.7
p-MeO-m-CN	184	-0.255	-0.7	27.5
p-*t*-Bu	185	-0.256	-0.08	14.4
m-Me	24.8	-0.069	0.00	1.46
p-MeS-m-CN	19.5	-0.043	-0.7	2.58
m-*c*-Propyl	19.0	-0.040	0.00	1.10
H	12.4	0.000	0.00	0.729

a) In 90% aq. acetone, 25°C. b) $\sigma^+ \equiv \log (k/k_H)/(-4.59)$ for cumyl solvolysis. c) In 80% aq. acetone, 45°C. d) Corrected for *isopolar* σ^+ value.

must be responsible to the higher resonance demand. It is important that the positions of these *isopolar* sets as well as the parent p-MeO and p-MeS groups spread over a wide range of σ^+ scale. Therefore, the resonance demand must be consistently higher in PhEt than cumyl system, for all the range of reactivity at least higher than the unsubstituted derivative.

The situation is clearly illustrated in Fig. 1, by the plot of PhEt[4a,b,9a] solvolysis data against σ^+ values from the cumyl solvolysis.[1,9b] The plot is no simple concave one expected for the gradual S_N1–S_N2 mechanistic transition, but a split pattern of three separate lines for meta groups, weak π-donors, and

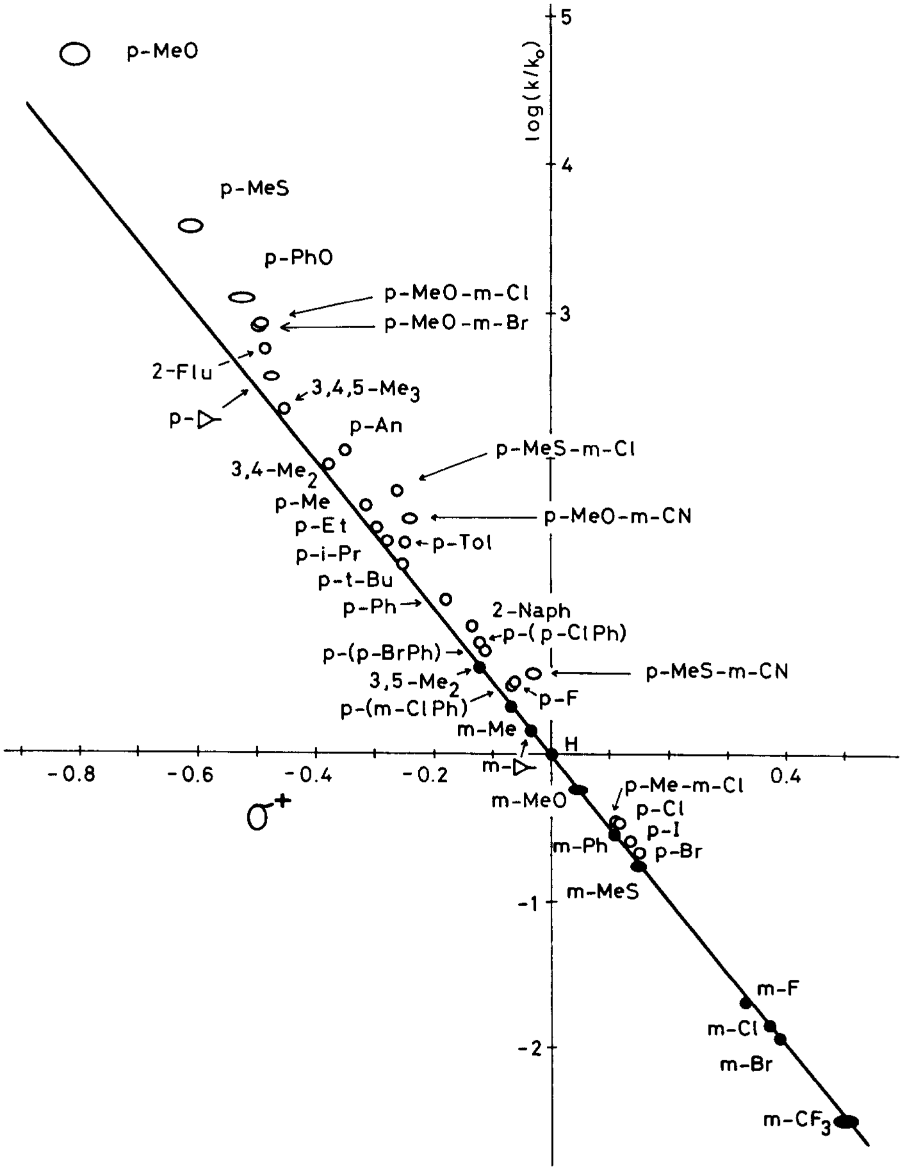

Fig. 1. σ^+ plot for the solvolysis of 1-phenylethyl chlorides.

strong π-donors including disubstituted ones. Vertical splittings at any σ^+ values are referred to the above *isopolar* comparison and are obviously a function of $\Delta\bar{\sigma}_R^+$ values. The split pattern is not in line with S_N1–S_N2 transition but with enhanced resonance demand of PhEt system. Generally, most σ^+ correlations so far involve a few typical strong p-π-donors. Because of the crude linearity between σ^+ and $\Delta\bar{\sigma}_R^+$ inherent in these p-π-donors, the stronger ones are localized at the most reactive end in 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 indistinguishable from the curvature associated with mechanistic shift. Thus it is worthy of note that the *isopolar* comparison or the deviation behavior of m-substituted π-donors disturbing the σ^+ *versus* $\Delta\bar{\sigma}_R^+$ linearity is most effective to distinguish the cause of non-linear σ^+ plot.

In the PhEt solvolysis, the effect of enhanced resonance demand evidently overweighs the non-linearity caused from mechanistic transition, even though the concurring S_N2 mechanism could not completely be ruled out for deactivating groups. For many, though not all, solvolysis reactions, the inadequacy of σ^+ scale may be an important cause of non-linear σ^+ correlations.

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