Tetrahedron Letters,Vol.24,No.21,pp 2177-2180,1983 0040-4039/83/212177-04$03.00/0
Printed in Great Britain

SUBSTITUENT EFFECT ON THE ACETOLYSIS OF 2-PHENYLETHYL TOSYLATE

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Abstract: The apparent substituent effect on the acetolysis of 2-arylethyl tosylates was analyzed as a sum of two linear substituent effect relationships for aryl-assisted and -unassisted processes. The effect on the former process satisfied the LArSR Eq. with a unique r value of 0.6.

In investigations of anchimerically assisted solvolyses, the effects of aryl substituents have played an important role as a measure of the significance of assistance.[1-3] Recently, we have reported[4] that the substituent effect on the acetolysis of neophyl brosylates can be described by a unique r value of 0.56 in our LArSR Eq.[5]

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

This appreciably exalted r value was taken as evidence for a direct π-delocalization interaction between the aryl π-system and β-carbocation center, *i.e.*, a bridged structure, in the rate-determining transition state.[5,6] While the r parameter is a sensitive measure of the resonance demands of varying systems, the results of LArSR analyses have led to the generalization that it shows little variation within a family of essentially the same mechanism and affords a unique value characteristic of the nature of the transition state of the system. It is therefore expected that the substituent effect on β-aryl assisted solvolyses can also be characterized by such a unique r value, contrary to the traditional σ^+ characterization.[3] Accordingly, this investigation was undertaken in an attempt to define more precisely the substituent effect on the anchimerically assisted (Fk_Δ) processes of β-arylalkyl solvolysis systems.

In most of such β-arylalkyl solvolyses, the precise analysis of substituent effects on the assisted process suffers from the mechanistic complexity due to the concurring aryl-unassisted (k_s) pathway, which even becomes predominant with the deactivating compounds.[1-3] The acetolysis of β-arylethyl tosylates chosen for the present study is no exception, and the solvolysis rate k_t ($= k_s + Fk_\Delta$) does not satisfy any simple linear substituent effect relationships. A useful way of separating rates of assisted process has been exploited by Schleyer, *et al.*,[2] based on the assumption of Hammett-type relationships for respective pathways, practically observable in extreme cases, $Fk_\Delta \gg k_s$ and $k_s \gg Fk_\Delta$.

$$\log(k_t^X/k_t^H) = \rho_s\bar{\sigma}_s + \log(k_s^H/k_t^H) \quad \text{for } k_s \text{ process } (k_s >> Fk_\Delta)$$

and

$$= \rho_\Delta\bar{\sigma}_\Delta + \log(Fk_\Delta^H/k_t^H) \quad \text{for } Fk_\Delta \text{ process } (Fk_\Delta >> k_s)$$

While a reasonable Hammett correlation was in fact obtained for the k_s process,[2] data were not sufficient to define the correlation for the Fk_Δ process. Data for β-arylethyl solvolysis have now become available covering an extended range of substituents (Table 1) including disubstituted compounds which were found to be particularly effective for defining the r for the neophyl system.[4]

The substituent effect on the k_s process may be treated simply with σ^o, since the process involves no direct π-interaction between the aryl and reaction site. This permits the evaluation of Fk_Δ values, and the substituent effect can be analyzed in terms of the LArSR Eq. (1). While a precise analysis can be achieved by the iterative least squares procedure,[7] direct graphical examination appears to be important in order to understand the nature of the Fk_Δ substituent effects. For simplicity, taking r as the constant of the Fk_Δ processes, the apparent $\bar{\sigma}_{NP}$ values derived from neophyl acetolysis[4] are used in Fig. 1 as a reference $\bar{\sigma}_\Delta$ set of an appropriate r, in comparison with the ordinary σ^+ ($r = 1.0$).

The key principle of the present 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 correlation lines at either activating or deactivating end. It should be noted that para π-acceptor as well as meta substituents can unequivocally define the non-linear k_t correlation in terms of standard σ^o constants, since only para π-donors are susceptible to resonance demands, *i.e.*, to the r value, in electrophilic resonance reactions. The k_s correlation can be defined

Table 1. Acetolysis of β-Arylethyl Tosylates at 115.00°C

Subst.	$10^5k_t^X$ (s^{-1})	k^X/k^H	Subst.	$10^5k_t^X$ (s^{-1})	k^X/k^H
p-OCH_2CH_2-m	133[a]	102	p-Ph	1.903	1.45
p-MeO-m-Me	91.0[a]	69.5	m-Me	1.62[b]	1.28[c]
p-MeO	43.4	33.2	H	1.309	1.00
3,4,5-Me_3	10.26	7.84	p-MeS-m-Cl	1.196	0.914
2-Fluo.	7.00[b]	5.51[c]	p-F	1.186	0.906
p-PhO	6.86	5.24	p-Cl	0.845[b]	0.665[c]
3,4-Me_2	6.37	4.87	m-F	0.761[b]	0.599[c]
p-MeS	5.43	4.15	m-Cl	0.728[b]	0.573[c]
p-Me	3.892	2.97	m-CF_3	0.689[b]	0.543[c]
p-t-Bu	3.56	2.72	p-CF_3	0.699[b]	0.550[c]
p-MeO-m-Cl	3.275	2.50	p-NO_2	0.635[b]	0.500[c]
3,5-Me_2	2.322	1.77	3,5-$(CF_3)_2$	0.584[b]	0.460[c]

a) Arrhenius extrapolation. b) Lit. values.[2] c) Based on $k^H = 1.27 \times 10^{-5}$ (s^{-1}).[2]

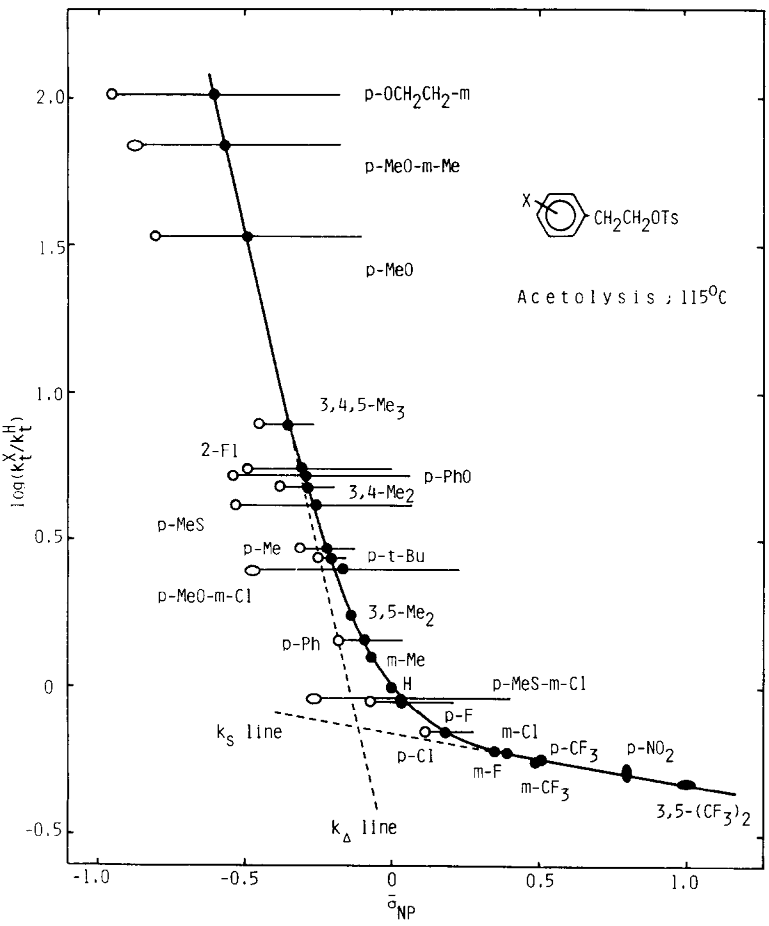

Fig. 1 The plot of log k_t^X/k_t^H against σ^+ and $\bar{\sigma}_{NP}$ constants.

unambiguously based upon deactivating substituents, giving a ρ_s value of -0.17. In contrast with the wide dispersion of σ^+ plots (open circles), the plots (closed circles) against $\bar{\sigma}_{NP}$ all collapse into a single smooth curve without any serious deviation. Activating substrates define fairly accurately the Fk_Δ line of $\rho_\Delta \cong -4$ bound smoothly to the k_t curve determined by r-independent substituents. In addition, the Fk_Δ and k_s correlation lines cross each other at the point 0.30 log-unit below the k_t line, as expected for $k_s = Fk_\Delta = k_t/2$. No reasonable Fk_Δ correlation line appears to be drawn through σ^+ plots. Both correlations are contrasted sharply by the behavior of less activating strong π-donors, such as p-MeO-m-Cl and p-MeS-m-Cl derivatives.[8] There is no doubt that the $\bar{\sigma}_{NP}$ of $r = 0.56$ is far more suitable than σ^+ ($r = 1.00$) for the Fk_Δ correlation. The best-fit r value does not appear to differ so significantly from that of $\bar{\sigma}_{NP}$. Now we can define the substituent effect on the Fk_Δ pathway in terms of this unique r value of about 0.6.[7,8]

Finally, it should be emphasized that the aryl-assisted process of phenylethyl acetolysis is a complex process involving significant return from the phenonium intermediate,[9] in contrast with the neophyl solvolysis. Such a mechanistic complexity has often been the cause of disagreement concerning the deviation of r from unity against our LArSR concept of varying resonance demands.[10] The apparent substituent effect on the phenylethyl Fk_Δ process might not be the intrinsic effect on the k_Δ ionization but a modified one associated with the substituent-change in F value. However, the same r value for both assisted processes is not in line with any argument based on a constant resonance demand $r = 1.00$. Further, accumulated data indicate that the F value is remarkably constant, independent of aryl substituents.[9] The reduced r value of 0.6 must be inherent in the process of rate-determining ionization through a β-aryl-assisted transition state.

References and Notes

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(Received in Japan 21 February 1983)