SUBSTITUENT EFFECT ON THE ACETOLYSIS OF NEOPHYL p-BROMOBENZENESULFONATES

Yuho Tsuno,* Kimito Funatsu, Yasuyuki Maeda, Masaaki Mishima, and Mizue Fujio
Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Fukuoka 812, Japan

Abstract:  The substituent effect on the acetolysis of neophyl brosylates was
analyzed successfully based on the analysis method of Yukawa-Tsuno.  The basic
concept of this method was strongly supported.

The substituent effect on the acetolysis of 2-aryl-2-methyl-1-propyl
(neophyl) brosylates was studied earlier by Heck and Winstein[1] for a limited
number of substituents and shown to give a reasonably good correlation with $\sigma^+$
rather than $\sigma$ constants, which was taken as evidence for the anchimeric assist-
ance of $\beta$-aryl group.[1,2]  Previously, we showed that this set was described most
reasonably with our LArSR (Yukawa-Tsuno) equation but not with simple $\sigma^+$ treat-
ment, and emphasized that the unique r value could be referred to the different
mode of resonance stabilization of the transition state from that of cumyl
chloride solvolysis.[3]  Additional data later reported, especially for deactivat-
ing substituents, provided further support for the LArSR treatment.[4,5]  The LArSR
analysis was applied generally to substituent effects on neighboring aryl-
assisted solvolyses, to give most cases comparable r value with that for neophyl
solvolysis.[2,6,7]  Thus the acetolysis of neophyl brosylates has been an espe-
cially important set in our continued investigations of general substituent
effects.  What we have envisaged in the LArSR Eq. (1) is that the r value varies
with reactions reflecting the different charge delocalization into aryl ring at
the transition state.[6]

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

Recently Johnson carried out a critical test of the validity of LArSR equa-
tion and cast doubts on the significance of r value as a measure of resonance
demands.[8]  Although his conclusion has also been criticized by others,[9] it
appears now necessary to clarify our position and to answer the question whether
our basic LArSR concept of varying demands on resonance effects with different
systems is valid.  Since the acetolysis of neophyl brosylates gives a unique
r value significantly different from unity or zero, this set would be most
appropriate to reexamine the validity of LArSR treatment.  Accordingly, we have
determined the acetolysis rates for several important substituents and carried
out detailed analysis of the substituent effect in terms of Eq. (1).  In the

present paper we wish to report the results of analysis as evidence for the validity of the LArSR assumption.

Rate constants of the acetolysis of substituted neophyl brosylates are summarized in Table 1, together with literature values.[1,4] Figure 1 shows the plot of log $(k/k_o)$ against $\sigma^0$ and $\sigma^+$. The relative rate does not follow the sequence of $\sigma^+$ constants. Only with meta substituents and p-$\pi$-acceptors a good linear relationship is constructed, the range of which ca. $10^4$ in reactivity is wide enough to define a $\rho_m$ value of $-3.899 \pm 0.057$ for this system. In the $\sigma^+$ plot, all the $\pi$-donors fall below the meta line and in particular strong $\pi$-donors including disubstituted ones[10] fall on a separate line parallel to the meta line over a range of $10^4$ in reactivity. The gap of one log-unit between two lines exceeds the ordinary limit of uncertainty. The weak $\pi$-donors also run parallel over a $10^3$ range but with a smaller gap. Obviously, the simple $\sigma^+$ treatment fails to describe the present data set with satisfactory precision.

The LArSR correlation contrasts sharply with the poor one given by $\sigma^+$. In the figure the stretches between $\sigma^+$ and $\sigma^0$ values for para $\pi$-donor substituents illustrate their resonance capabilities, i.e., $\Delta\bar{\sigma}_R^+$ values. The $\rho_m$ correlation line intersects all the stretches at the points giving a constant ratio of 2:3, which refers to the r value of this system. Least squares application of the Eq. (1) affords an excellent correlation (indicated by squares in Fig. 1)

$$\log (k/k_o) = (-3.871 \pm 0.038)(\sigma^0 + 0.563\Delta\bar{\sigma}_R^+)$$

with correlation coefficient 0.99968 (n = 19) and standard deviation $\pm 0.041$. m,p-Disubstituted derivatives also satisfy this relationship, based on the

Table 1        Acetolysis of Neophyl Brosylates at 75.00°C

| Subst. | $10^5 k$ (s$^{-1}$) | $k/k_o$ | Subst. | $10^5 k$ (s$^{-1}$) | $k/k_o$ |
|---|---|---|---|---|---|
| p-OCH$_2$CH$_2$-m | 1560[a] | 217 | H | 7.20 | 1.00 |
| p-MeO-m-Me | 1160[a] | 161 | p-MeS-m-Cl | 5.90 | 0.819 |
| p-MeO | 577[a] | 80.1 | p-F | 5.376 | 0.747 |
| m,p-Me$_2$ | 103.2 | 14.33 | m-MeO | 4.75[b] | 0.694[d] |
| p-C$_6$H$_5$O | 96.8[a] | 13.44 | p-Cl | 1.409 | 0.1957 |
| p-MeS | 71.2[a] | 9.89 | p-Br | 1.09[b] | 0.1594[d] |
| p-Me | 50.7 | 7.04 | m-Cl | 0.219[a] | 0.0304 |
| p-t-Bu | 46.3 | 6.43 | p-COOMe | 0.132[b] | 0.0193[d] |
| p-MeO-m-Cl | 32.7 | 4.54 | m,p-Cl$_2$ | 0.0897[a] | 0.0125 |
| p-C$_6$H$_5$ | 16.68 | 2.317 | p-CN | 0.0191[a,c] | 0.00279[d] |
| m-Me | 13.18[b] | 1.927[d] | p-NO$_2$ | 0.0055[a,c] | 0.00080[d] |

a) Extrapolated from the rate constants at other temperatures.  b) Ref. 1.
c) Ref. 4.  d) Based on $6.84 \times 10^{-5}$ s$^{-1}$ for the unsubstd. compound (ref. 1).

assumption of additivity of substituent effects.[10]

The LArSR results are consistent with the accepted mechanism, in which the reaction proceeds through a rate-determining bridged transition state and cascades down to the tertiary carbonium ion.[3,11] The exalted r value of 0.56 provides evidence for the direct π-interaction between aryl π-system and the β carbonium center at the rate-determining transition state, and suggests that considerable positive charge is delocalized into the β-aryl ring but the delocalization is less effective than in the cumyl solvolyses. The large ρ value is also in line with the bridged transition state.

It should be emphasized that this precise LArSR relationship may be indicative of the absence of appreciable mechanistic change within the range of the substituent change. The absence of mechanistic change is the basic requirement of linear free energy relationship analysis. On the other hand, the $\sigma^+$ correlation can be regarded as a curve or a bisected one, at least for typical substituents on which previous analyses were based. This is serious because the curvature might be associated with mechanistic change.[12] It was pointed out that the improvement of correlation with LArSR treatment in such a case should not have any theoretical significance.[12] The difficulty arises mostly from the fact that the strong π-donors at the most reactive end deviate in a similar manner with



the change in mechanism as well as resonance demand. However, since the mechanistic change should also be a simple function of substituent constants, the plot must be smooth-curved or bilinear against only appropriate substituent constants.[13] Therefore, the significant deviations of strong π-donors in the middle of the plot are particularly noteworthy. The split pattern of the $\sigma^+$ plot is clearly inconsistent with any argument based on mechanistic shift. As a consequence, it can be concluded that the r value of 0.56 is not due to the change in mechanism.

Johnson suggested an alternative interpretation that the overall reaction conforming to the LArSR Eq. 1 with any intermediate r value is of two steps, a preequilibrium and a rate-determining step, one of which correlates with $\sigma^0$ (or $\sigma$) and

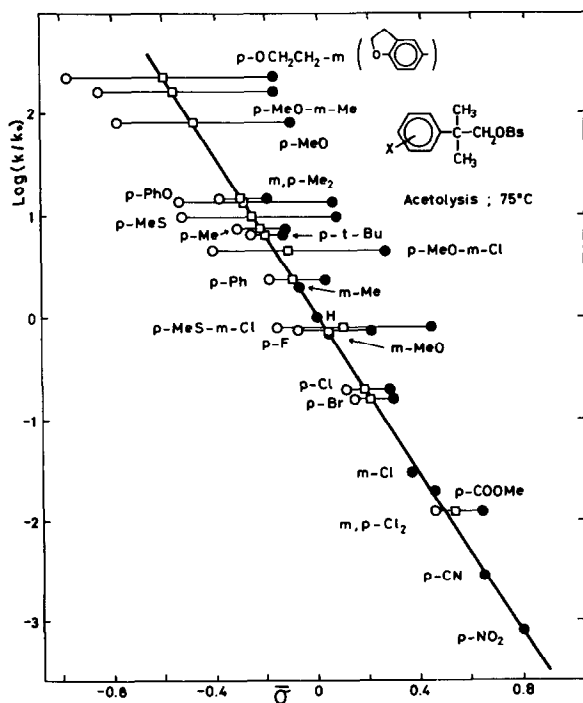Fig. 1   The plot of log $k/k_0$ against $\sigma^+$ and $\sigma^0$ constants.

the other with $\sigma^+$.[8] The preequilibrium aryl-assisted ionization is not in line with the accepted mechanism of this reaction, since no return from the phenonium intermediate is occurring.[2] The only conceivable multi-step mechanism is one involving the ionization to primary-neophyl ion followed by the rearrangement (aryl-assisted) process.[11] While the former step may be reasonably referred to $\sigma^0$ and the latter presumably to $\sigma^+$ term, the Johnson scheme requires for the enhanced r value that the second $\sigma^+$-dependent step must be rate-determining; or otherwise, the apparent substituent effect should be $\sigma^0$-dependent.[14] It seems however highly unlikely that the unassisted ionization ($k_c$) into an unstable primary ion occurs energetically more easily than the rearrangement to a far stable tertiary ion.[7] In any case, the preequilibrium scheme does not appear to apply to the present reaction.

In conclusion the intermediate r value of this reaction must be referred to the nature of the aryl-assisted transition state in the accepted mechanism. Thus, our LArSR concept of varying resonance demand is evidently supported. There are many reactions of essentially single rate-determining step requiring the r value of neither unity nor zero. The r value has physical significance as a coefficient measuring the importance of $\pi$-delocalization interaction between the ring $\pi$-system and reaction site at the rate-determining transition state.

Full discussion will be presented in subsequent papers.

### References and notes

1) R. Heck and S. Winstein, J. Am. Chem. Soc., 79, 3432 (1957).   2) C. L. Lancelot, D. J. Cram, and P. v. R. Schleyer, "Carbonium ions," ed by G. A. Olah and P. v. R. Schleyer, Wiley-Interscience, New York (1972), Vol. 3, Chap. 27, 1347.   3) Y. Yukawa and Y. Tsuno, Bull. Chem. Soc. Jpn., 32, 971 (1959).   4) H. Tanida, T. Tsuji, H. Ishitobi, and T. Irie, J. Org. Chem., 34, 1086 (1969). 5) R. S. Bly, E. K. Ni, A. K. K. Tse, and E. Wallace, J. Org. Chem., 45, 1362 (1980); M. G. Jones and J. L. Coke, J. Am. Chem. Soc., 91, 4284 (1969).   6) Y. Yukawa, Y. Tsuno, and M. Sawada, Bull. Chem. Soc. Jpn., 39, 2274 (1966); Y. Tsuno, Y. Kusuyama, M. Sawada, T. Fujii, and Y. Yukawa, ibid., 48, 3337 (1975). 7) F. L. Schadt Ⅲ, C. J. Lancelot, and P. v. R. Schleyer, J. Am. Chem. Soc., 100, 228 (1978).   8) C. D. Johnson, J. Org. Chem., 43, 1814 (1978).   9) J. S. Lomas and A. Argile, J. Org. Chem., 44, 2024 (1979); R. Taylor, ibid., 44, 2024 (1979).   10) Simple additivity was assumed for either $\sigma^0$ or $\sigma^+$ constants, and the $\Delta\bar{\sigma}_R^+$ values were given to be equal to those of para substituents. 11) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, J. Am. Chem. Soc., 89, 370 (1967).   12) J. Shorter, "Correlation  Analysis in Chemistry," ed by N. B. Chapman and J. Shorter, Plenum Press, New York (1978), Chap. 4, 119.   13) P. G. Gassman and A. F. Fentiman, Jr., J. Am. Chem. Soc., 92, 2549 (1970).   14) However see ref. 11.