# Exalted Resonance Effect in the Aryl-Assisted Solvolyses of 2-Aryl-2-(trifluoromethyl)ethyl *m*-Nitrobenzenesulfonates

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(Received June 26, 1997; CL-970488)

The substituent effects on solvolysis of 2-aryl-2-(trifluoromethyl)ethyl *m*-nitrobenzenesulfonates, in acetic acid and in 80% aqueous trifluoroethanol, were analyzed by Yukawa-Tsuno equation. The resonance demands ($r$ = 0.77 in acetic acid) were larger than that of standard aryl-assisted solvolysis by 0.2. This enlargement should depend on a destabilization of aryl-assisted transition-state by an electron-withdrawing trifluoromethyl group.

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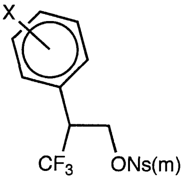
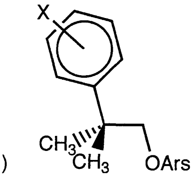
The nature of carbocations that are destabilized by strongly electron-withdrawing substituents has been studied actively.[1] Because of our interest in aryl-assisted solvolysis of 2-arylalkyl systems[2] via intermediate phenonium ion[3,4] which have been a matter of intense investigation since Cram's work,[4] we attempted to examine the solvolyses of 2-aryl-2-(trifluoromethyl)ethyl system where the phenonium ion intermediate must be destabilized by trifluoromethyl ($CF_3$) group. The substituent effect in aryl-assisted solvolysis ($k_\Delta$), where the direct π-interaction exists between 2-aryl and carbocationic reaction center, can be generally described by Yukawa-Tsuno Eq. (1).[5]

$$\log (k_X/k_H) = \rho(\sigma^o + r\Delta\bar{\sigma}_R^+) \qquad (1)$$

While an intermediate $r$ value (0.63 - 0.40) has been observed in the $k_\Delta$ solvolyses,[6-8] an enlarged $r$ value was expected in our system since the solvolysis of extremely deactivated benzylic substrates with a $CF_3$ group at the reaction site has been characterized by a remarkably high resonance demand.[9] The analysis of relationship between the deactivation and the $r$ value was main purpose of our study.



**1**



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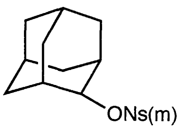

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The *m*-nitrobenzenesulfonates (nosylates) **1** were prepared by the ordinary Tipson method[10] from the alcohols which were obtained by reduction of 2-aryl-3,3,3-trifluoropropionic acid with $LiAlH_4$. The 2-aryl-3,3,3-trifluoropropionic acids were prepared from aryl trifluoromethyl ketones by Mosher's procedures.[11]

Solvolysis of primary and secondary β-arylalkyl derivatives proceeded *via* two independent pathways: aryl-assisted ($k_\Delta$) and solvent-assisted ($k_S$), and the $k_\Delta$ process was enhanced by electron-releasing substituents (*e.g.*, *p*-MeO).[12] Thus, solvolysis rates of *p*-methoxy derivative **1a** were determined in a wide variety of solvents by conductometric method,[13] as shown in Table 1, in order to check the reaction mechanism by analysis of solvent effect. In Figure 1, the solvolysis rates of **1a** are plotted, on a logarithmic scale, against the corresponding rates of 2-adamantyl nosylate **3**. The 2-adamantyl $Y_{ONs}$ parameter[14] apparently gave no simple linear relationship for **1a**. This split pattern appeared to be quite similar to that of neophyl substrates **2** which were typical examples of the aryl-assisted solvolysis.[13] The plots for less nucleophilic solvents, aq trifluoroethanol, lay above the aq ethanol (nucleophilic solvents) line. The pattern of deviation was inconsistent with that expected for mechanistic involvement of the solvent nucleophilicity. Certainly the solvolysis of **1a** was proceeding by the $k_\Delta$ process without the competing $k_S$ process.

**Table 1.** Rate constants[a] ($k$) of solvolysis of 2-(*p*-methoxyphenyl)-2-trifluoromethylethyl nosylate in aq solvents at 75 °C

| Solvent[b] | $Y_{ONs}$[c] | $k/10^{-5}s^{-1}$ | Solvent[b] | $Y_{ONs}$[c] | $k/10^{-5}s^{-1}$ |
|---|---|---|---|---|---|
| 80E | 0.000 | 0.755 | 60A | 0.331 | 0.631 |
| 70E | 0.401 | 1.32 | 50A | 0.857 | 1.24 |
| 60E | 0.782 | 1.93 | 40A | 1.387 | 2.08 |
| 50E | 1.154 | 2.45 | 30A | 1.948 | 4.23 |
| 40E | 1.619 | 3.27 | 97Tw | 1.148 | 3.01 |
| 30E | 2.173 | 5.10 | 80T | 1.225 | 3.18 |
| 70A | -0.196 | 0.341 | 50T | 1.508 | 3.70 |

[a]Followed conductimetrically. Errors were max. 5 %. [b]Volume% of organic solvent excluding 97 Tw (weight%). Abbreviation; E=EtOH, A=acetone, T=TFE=trifluoroethanol. [c]Reference 12.

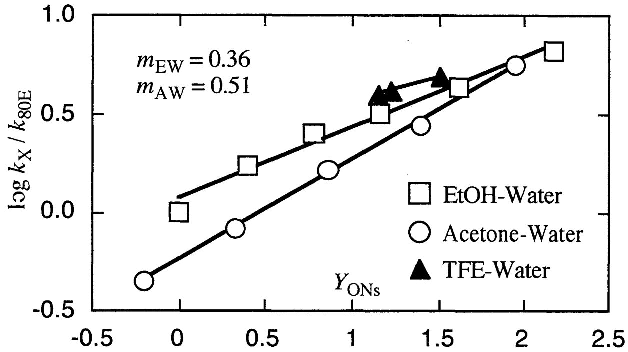

**Figure 1.** The $mY_{ONs}$ plots of solvent effect for the solvolyses of 2-(*p*-methoxyphenyl)-2-trifluoromethylethyl nosylate at 75 °C.

The substituent effects on solvolysis rates were analyzed by using a minimum basis data set to confirm the resonance demand. The set involved *p*-methoxy-*m*-chloro substituent that is efficient to determine the $r$ value accurately because it has a high resonance effect ($\Delta\bar{\sigma}_R^+$ = –0.69) although the inductive effect is electron-withdrawing ($\sigma^o$ = 0.22).[6,9a] The solvolyses, in 80% (v/v)

**Table 2.** Rate constants ($k$) of solvolysis of nosylates **1**

| Solvent$^a$ | $Y_{ONs}$$^a$ | Temp /°C | $p$-MeO<br>$k$/$10^{-5}s^{-1}$ | $p$-Me<br>$k$/$10^{-5}s^{-1}$ | $p$-MeO-$m$-Cl<br>$k$/$10^{-5}s^{-1}$ | H<br>$k$/$10^{-5}s^{-1}$ |
|---|---|---|---|---|---|---|
| 80T | 1.225 | 100 | 25.7 | 1.87 | 1.26 | 0.133 |
| AcOH | -1.052 | 130 | 17.5 | 0.934 | 1.44 | 0.180 |

$^a$See Table 1.

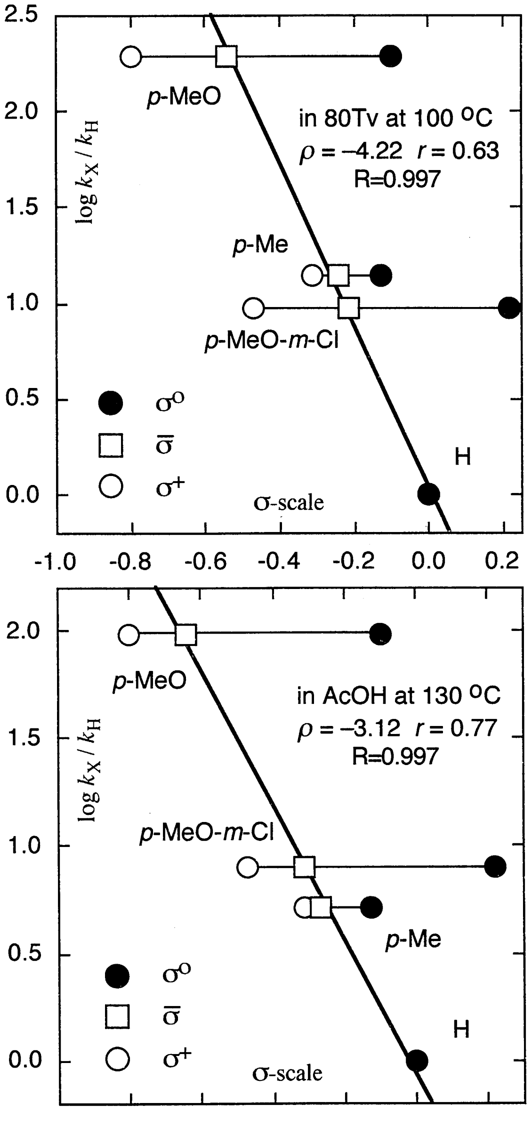

**Figure 2.** Yukawa-Tsuno plots for the solvolyses of 2-aryl-2-$CF_3$-ethyl nosylates in 80% TFE-d3 / 20% $D_2O$ at 100 °C and in AcOH-d4 at 130 °C.

trifluoroethanol-$d_3$ / $D_2O$ at 100 °C and in acetic acid-$d_4$ at 130 °C, were followed to 3 half-lives reaction by $^1H$ NMR.[15] The aryl-unmigrated primary alcohol or acetate was only produced, and the decrease of substrate obeyed good first-order kinetics. The rate data are summarized in Table 2. Figure 2 shows the Yukawa-Tsuno plots of the results, and good linear correlations are observed in both plots over an all range. Accordingly it was concluded that the solvolyses of four derivatives **1** are proceeding by the same mechanism, that is $k_\Delta$. The large $\rho$ ($\leq$–3.1) and $r$ ($\geq$0.63) values confirm the $k_\Delta$-mechanism where the direct $\pi$-interaction exists between aryl and reaction site. Therefore we can discuss the resonance demand of aryl-participation that gives a phenonium-ion intermediate.

Although a solvent dependence of $r$ value was observed, i.e. 0.63 in 80T and 0.77 in AcOH, both $r$ values were larger by 0.2 than that of neophyl system **2** (0.43 in 80T, 0.57 in AcOH)[6,7] respectively. These enlargements should depend on the destabilization of aryl-assisted transition-state by an electron-withdrawing trifluoromethyl group. Indeed, the acetolysis of **1a** was retarded $1.3\times10^2$ and $1.5\times10^4$ times compared to that of 2-($p$-methoxyphenyl)ethyl and $p$-methoxyneophyl derivatives, respectively.[7,8,16] The solvent effect on $r$ value was also explained by the change of the transition-state stability, that is, the $r$ value decreases with the increased stability by solvent ionizing power.[7]

This is the first report on highly destabilized aryl-assisted solvolysis. Further investigation on the structure of transition-state and the solvolyses of other deactivated $\beta$-arylalkyl esters are now in progress.

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