

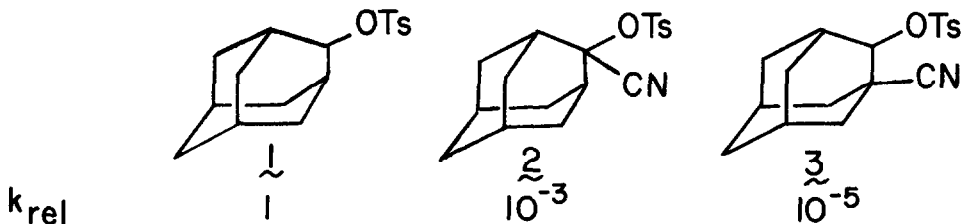
H/ α -CN VERSUS H/ β -CN RATE RATIOS IN THE SOLVOLYSIS
OF SULFONATE ESTERS IN UNCONSTRAINED SYSTEMS.
ADDITIONAL EVIDENCE FOR CONJUGATIVE STABILIZA-
TION OF ATTACHED CARBOCATIONS BY THE CYANO MOIETY

Paul G. Gassman* and Katsuhiro Saito
Department of Chemistry, University of
Minnesota, Minneapolis, Minnesota 55455

Summary: H/ α -CN and H/ β -CN rate ratios have been measured for the solvolysis of sulfonate esters of relatively simple, noncyclic aliphatic alcohols. The β -CN function was found to be far more rate retarding than the α -CN function.

In general, physical organic chemists attempt to avoid writing reaction mechanisms which require the placement of a positive charge on carbons attached to strong electron-withdrawing groups. However, this tendency is primarily intuitive; little experimental data exist which support this approach. Recently, we have become very involved in evaluating the interaction of strong electron-withdrawing substituents on directly attached carbocations.^{1,2} These studies have shown that mechanistic speculation is often based on a mental extrapolation of β -substituent effects³ and that these extrapolations may be misleading due to major conjugative interactions. This would appear to be the situation for the cyano group.^{1,2d}

In an attempt to compare the effect of α - vs. β -cyano groups on the generation of an incipient cationic species, we have recently compared the rate ratios of λ - λ .^{1d} As would be predicted on the basis of our earlier studies,^{1a-c} the β -cyano group was more rate retarding than the α -cyano group.



This has been rationalized as being the result of a major resonance stabilization by λ when the cyano function was in the α -position. Because of the rigid structure of the adamantyl skeleton, it was difficult to ascertain what, if any, through space polar interaction the cyano group of λ might have with the incip-

ient cationic center.⁴ Thus, a study of the effect of cyano functions in non-

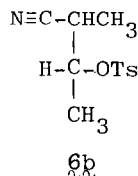
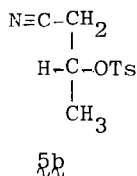


constrained systems was desirable. We now wish to report the results of such an investigation which uses simple noncyclic aliphatic hydrocarbons as substrates.

Table 1 lists the rates of solvolysis of a series of sulfonate esters in anhydrous 2,2,2-trifluoroethanol buffered with 2,6-lutidine.⁵ As can be seen from the Table, the slowest relative rate observed was that of $7b$ which had a cyano group in the β -position. Comparison of 7 with $7b$ showed a rate retardation by the β -cyano function of 7.9×10^7 . This would imply that in 3 and in other systems where β -cyano effects on solvolysis have been measured,^{3c-f} the inductive effect was not maximized.

Comparison of the sulfonate pairs $5/5a$, $6/6a$, $7/7a$, and $8/8a$ gave H/ α -CN rate ratios of 3.51×10^3 , 1.55×10^3 , 5.15×10^3 , and 3.15×10^3 , respectively. It is clear from this series that the rate retarding influence of an α -cyano substituent is orders of magnitude less than the effect of a related β -cyano group. A comparison of $7a$ with $7b$ gives an α -CN/ β -CN rate ratio of 1.53×10^4 .

H/ β -CN rate ratios could not be obtained for either system 5 or system 6 due to the involvement of an E2 elimination. In contrast to the rates for all of the compounds in Table 1, the rates of acid generation from $5b$ and $6b$ were extremely dependent on buffer concentration. Thus, it would appear that the presence of the β -cyano group of $5b$ and $6b$ was sufficient to cause a shift in mechanism from carbonium ion generation (S_N1) to concerted elimination (E2). This held for 2,6-lutidine, 2,6-di-t-butylpyridine, and sodium acetate as



buffers.

Product studies showed that all of the compounds in Table 1 gave olefins as the major products.⁶

Acknowledgement. We are indebted to the National Science Foundation for Grant CHE78-10231 which supported this investigation.

Table 1. Rates of Solvolysis of Sulfonate Esters in 2,2,2-Trifluoroethanol Buffered with 2,6-Lutidine.

Compound	$k(25.0^\circ\text{C})^a$	ΔH^\ddagger	ΔS^\ddagger	k_{rel}
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{C}-\text{OTs} \\ \\ \text{CH}_3 \end{array}$ <p>5</p>	7.89×10^{-7b}	19.1 ± 0.2	-22.3 ± 0.5	3.79×10^6
$\begin{array}{c} \text{CH}_3 \\ \\ \text{N}\equiv\text{C}-\text{C}-\text{OTs} \\ \\ \text{CH}_3 \end{array}$ <p>5a</p>	2.24×10^{-10b}	27.5 ± 1.5	-10.5 ± 3.6	1.08×10^3
$\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ \text{H}-\text{C}-\text{OTs} \\ \\ \text{CH}_3 \end{array}$ <p>6</p>	1.32×10^{-6}	21.7 ± 0.1	-12.7 ± 0.3	6.35×10^6
$\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ \text{N}\equiv\text{C}-\text{C}-\text{OTs} \\ \\ \text{CH}_3 \end{array}$ <p>6a</p>	8.53×10^{-10}	26.5 ± 0.1	-11.0 ± 0.1	4.10×10^3
$\begin{array}{c} \text{CH}(\text{CH}_3)_2 \\ \\ \text{H}-\text{C}-\text{OTs} \\ \\ \text{CH}_3 \end{array}$ <p>7</p>	1.64×10^{-5}	19.9 ± 0.1	-13.8 ± 0.3	7.88×10^7
$\begin{array}{c} \text{CH}(\text{CH}_3)_2 \\ \\ \text{N}\equiv\text{C}-\text{C}-\text{OTs} \\ \\ \text{CH}_3 \end{array}$ <p>7a</p>	3.19×10^{-9}	24.9 ± 0.1	-13.8 ± 0.2	1.53×10^4
$\begin{array}{c} \text{N}\equiv\text{C}-\text{C}(\text{CH}_3)_2 \\ \\ \text{H}-\text{C}-\text{OTs} \\ \\ \text{CH}_3 \end{array}$ <p>7b</p>	2.08×10^{-13c}			1
$\begin{array}{c} \text{N}\equiv\text{C}-\text{C}(\text{CH}_3)_2 \\ \\ \text{H}-\text{C}-\text{OTf} \\ \\ \text{CH}_3 \end{array}$ <p>7b'</p>	3.58×10^{-8}	24.3 ± 0.1	-11.2 ± 0.2	

Compound	$k(25.0^\circ\text{C})^a$	ΔH^\ddagger	ΔS^\ddagger	k_{rel}
$\begin{array}{c} \text{C}(\text{CH}_3)_3 \\ \\ \text{H}-\text{C}-\text{OTs} \\ \\ \text{CH}_3 \\ \text{\textcircled{8}} \end{array}$	2.50×10^{-5}	21.3 ± 0.1	-7.9 ± 0.4	1.20×10^8
$\begin{array}{c} \text{C}(\text{CH}_3)_3 \\ \\ \text{N}=\text{C}-\text{C}-\text{OTs} \\ \\ \text{CH}_3 \\ \text{\textcircled{8a}} \end{array}$	7.94×10^{-9}	24.4 ± 0.2	-13.7 ± 0.6	3.82×10^4

(a) Extrapolated from higher temperatures. (b) Taken from ref. 1a.

(c) Compound $7b$ was too slow to measure at convenient temperatures. Thus, its rate was extrapolated from that of the corresponding triflate ($7b'$) by multiplying the rate of $7b'$ by 5.8×10^{-6} . This ratio represents the measured rate difference between $5a$ and the corresponding triflate ($5a'$).

References and Footnotes

- (a) P.G. Gassman and J.J. Talley, *J. Am. Chem. Soc.*, **102**, 1214 (1980); (b) P.G. Gassman and J.J. Talley, *ibid.*, **102**, 4138 (1980); (c) D.A. Dixon, P.A. Charlier, and P.G. Gassman, *ibid.*, **102**, 3957 (1980); (d) P.G. Gassman, K. Saito, and J.J. Talley, *ibid.*, in press.
- For recent related experimental and theoretical studies, see (a) X. Creary, *J. Org. Chem.*, **44**, 3938 (1979); (b) K.M. Koshy and T.T. Tidwell, *J. Am. Chem. Soc.*, **102**, 1216 (1980); (c) K.-T. Liu and C.-F. Sheu, *Tetrahedron Lett.*, 4091 (1980); (d) M.N. Paddon-Row, C. Santiago, and K.N. Houk, *J. Am. Chem. Soc.*, **102**, 6561 (1980).
- For selected examples of β -substituent effects, see: (a) P.G. Gassman, J.L. Marshall, J.G. Macmillan, and J.M. Hornback, *J. Am. Chem. Soc.*, **91**, 4282 (1969); P.G. Gassman and J.G. Macmillan, *ibid.*, **91**, 5527 (1969); P.G. Gassman, J.L. Marshall, and J.M. Hornback, *ibid.*, **91**, 5811 (1969); (b) P.G. Gassman and J.M. Hornback, *ibid.*, **91**, 5817 (1969); (c) R. Muneyuki and T. Yano, *ibid.*, **92**, 746 (1970); (d) J.B. Lambert and A.G. Holcomb, *ibid.*, **93**, 2994 (1971); J.B. Lambert and H.W. Mark, *ibid.*, **100**, 2501 (1978); (e) D. Farcasiu, *ibid.*, **98**, 5301 (1976); D. Farcasiu, *J. Org. Chem.*, **43**, 3878 (1978); (f) D. Lenoir, *Tetrahedron Lett.*, 1563 (1974).
- The same problem exists with other systems in which the β -cyano effect has been studied.^{3c,f}
- All rates were measured conductimetrically and showed excellent first-order kinetics through at least three half lives. The rates shown were independent of buffer concentration over a significant range.
- Detailed product analyses and the synthetic details of all of the compounds in Table 1 will be presented in a full paper on this subject.

(Received in USA 11 December 1980)