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Solvolysis of 1-Phenyl-1-cyano-2,2,2-trifluoroethyl Brosylate¶

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The rates of solvolysis of 1-phenyl-1-cyano-2,2,2-trifluoroethyl brosylate were measured in various solvents, and the solvent effect was analyzed on the basis of Winstein-Grunwald Eq., giving m=0.88 and l=0.49.

The solvolytic behavior of destabilized carbocations with strongly electron-withdrawing α-substituents has received considerable attention as an extended field of the carbocation chemistry.$^{1-7)}$ The solvolysis of 1-phenyl-1-(trifluoromethyl)ethyl tosylate (**1**) shows a remarkable rate decrease of the order of 10^{-4} - 10^{-6} for the α-trifluoromethyl group relative to α-hydrogen, but shows typical k_c behavior suggesting the intermediacy of highly destabilized carbocation.$^{2-3)}$ Gassman observed the deceleration effect of approximately 10^{-3} for the α-CN in 1-phenyl-1-cyanoethyl substrates (**2**), but argued for the high carbocationic character of the solvolysis.$^{4)}$ Similar destabilized carbocation intermediates have been considered for the reactions of deactivated secondary benzylic substrates.$^{5)}$ A mechanistic probe to establish the intermediacy of carbocationic intermediates in solvolysis processes should be a large response of the rate to the solvent polarity.$^{1-7)}$ The Winstein-Grunwald Eq. 1 has been widely used for this purpose,$^{8)}$

$$\log k/k_0 = m\,Y + l\,N \qquad (1)$$

The solvolysis of **1** was reported to follow Eq. 1 using Y_{OTs} based on 2-adamantyl tosylate solvolysis with a slope of $m \cong 1.0$, suggesting a limiting k_c mechanism for this reaction.$^{2)}$ However, the Y_{OTs} plot is not simply linear but significantly splits for various binary mixed solvent series, and the way of dispersion is not explicable by nucleophilic solvent participation. There have been no detailed studies on the solvent effect for the solvolysis of deactivated benzylic derivatives. We report here the solvent effect on the solvolysis of 1-phenyl-1-cyano-2,2,2-trifluoroethyl brosylate (**3**), doubly deactivated by CF_3 and CN groups at the α-position, and discuss the solvolysis mechanism of **3**, in comparison with relevant deactivated benzylic systems.

¶This paper is dedicated to late Professor Ryozo Goto, Kyoto University.

The rates of solvolysis of 3 were determined mostly by following the decrease in the UV absorption at 242 nm, in a series of solvents buffered with 1.5 equivalent 2,6-lutidine. The rate data are summarized in Table 1. The solvolysis rate of 3 was remarkably decelerated relative to 1 by a significant factor of 10^{-4}.

In Fig. 1 logarithmic rates for the solvolysis of 3 are plotted against Y_{OTs} values based on 2-adamantyl tosylate. The plot shows a linear correlation for aqueous ethanol and aqueous acetone series, but shows significant downward deviations for less nucleophilic solvents, aqueous TFE, HCOOH, HFIP, and CF_3COOH from the acetone-ethanol correlation line. The pattern of deviation is similar to that observed for k_s solvolyses involving nucleophilic solvent participation. 3 is less reactive by a factor of 10^{-5} than benzyl brosylate which reacts with appreciable nucleophilic participation at the reactant molecule,[8,9)] and may be considered to solvolyze by a mechanism involving significant S_N2 solvent participation. Application of Eq. 1 to 3 gives a correlation with m and l values of 0.88 and 0.49, respectively, in a precision of R=0.994 and SD=±0.09.[10)] It should be particularly noted that the solvolysis of 3 gave not only a large m

Table 1. Solvolysis of 1-Phenyl-1-cyano-2,2,2-trifluoroethyl Brosylate

Solvent a)	Rate/s^{-1} b) 25 °C	Rate/s^{-1} b) 45 °C	$\Delta H^{\ddagger}_{25\,°C}$ h) kcal mol^{-1}	$\Delta S^{\ddagger}_{25\,°C}$/e.u. h)
80% EtOH	1.32×10^{-8}	1.94×10^{-7}	24.7	-11.6
70% EtOH	3.06×10^{-8}	4.45×10^{-7}	24.6	-10.3
60% EtOH	7.73×10^{-8}	1.11×10^{-6}	24.4	-8.9
50% EtOH	1.76×10^{-7}	2.58×10^{-6}	24.7	-6.5
40% EtOH	4.79×10^{-7}	6.22×10^{-6} c)	23.5	-8.5
30% EtOH	2.27×10^{-6}	2.72×10^{-5}	22.8	-7.8
100% TFE	1.43×10^{-8}	1.99×10^{-7}	24.1	-13.3
70% TFEw d)	1.69×10^{-7}	2.43×10^{-6}	23.0	-12.3
50% TFE	2.09×10^{-7}	3.13×10^{-6}	24.9	-5.5
50% TFEw d)	2.28×10^{-7}	3.70×10^{-6}	25.6	-2.8
70% Acetone	7.56×10^{-9}	1.17×10^{-7}	25.2	-11.1
60% Acetone	2.80×10^{-8} g)	4.10×10^{-7}		
50% Acetone	9.17×10^{-8}	1.24×10^{-6}	23.9	-10.4
30% Acetone	1.55×10^{-6}	1.64×10^{-5} c)	21.7	-12.5
20% Acetone	4.43×10^{-6} g)	5.19×10^{-5} c)		
HCOOH e)	5.13×10^{-7}	7.70×10^{-6} c)	24.9	-3.7
CF_3COOH e,f)	2.44×10^{-7}	2.76×10^{-6}	22.2	-14.2
97% HFIPw d,e)	1.67×10^{-7} g)	2.26×10^{-6} c)		

a) Volume % of organic solvent. b) Calculated from data at higher temperatures. Solvents including 1.5 equiv. 2,6-lutidine, otherwise noted. c) Direct measurement. d) Weight % of organic solvent. e) Unbuffered. f) Reported $9.69 \times 10^{-8} s^{-1}$ at 25 °C, $\Delta H^{\ddagger}$=22.4 kcal mol^{-1}, and $\Delta S^{\ddagger}$=-15.6 e.u. (Ref. 6a). g) Based on log k-log k plot between 25 °C and 45 °C excluding 50% TFEw, HCOOH, and CF_3COOH. h) 1 cal= 4.184 J, 1 e.u. = 4.184 J $K^{-1}mol^{-1}$.

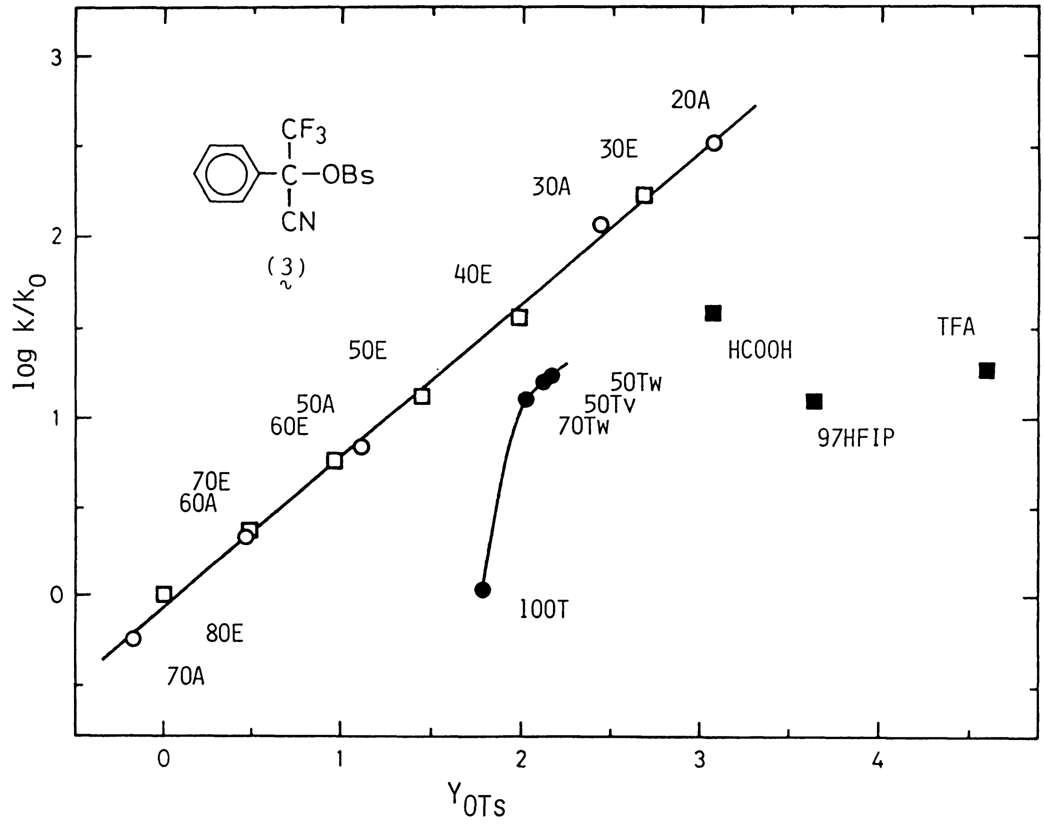

Fig. 1. The mY Plot of 1-Phenyl-1-cyano-2,2,2-trifluoroethyl OBs at 25 °C.

value but also a significant l value. Generally, in the ordinary k_s-k_c spectrum of solvolyses the m and l values tend to vary in a compensating way, i.e., $m + l \simeq 1$. The nucleophilic participation (l=0.49) is as significant as that in the solvolysis of 2-propyl tosylate8) (m=0.62, l=0.44), whereas the m value is similar to that of pinacolyl tosylate 8,11) which is thought to solvolyze by essentially limiting mechanism (m=0.85, l=0.08).9) The transition state of highly carbocationic character with significant solvent participation can hardly be figured out in terms of simple k_s-k_c solvolytic scheme of alkyl solvolysis. **3** may be solvolyzed through a highly charged transition state, despite the strong deactivation by two electron-withdrawing α-groups favoring nucleophilic solvent assistance.

Bentley et al.11) proposed "S_N2 intermediate" mechanism for the correlation with large m and l values for t-butyl chloride solvolysis. This may be applied to the present system. However, it is also likely that the highly crowded tertiary reaction center of **3** prevents the nucleophilic attack of solvent at the reactant, retaining the carbocation character of the transition state effectively high to give a large m value. Thus, an alternative interpretation will be that **3** reacts by initial ionization to form a carbocation (presumably an ion pair) intermediate, followed by rate-limiting product formation with solvent attack.2,5) The former step should be related only to the solvent ionizing power and the latter to the solvent nucleophilicity. While the Winstein-Grunwald analysis can not distinguish between both mechanistic assignments simply different in the timing of nucleophilic attack, it seems certain that the solvolysis of 3 may proceed through a highly cationic transition state, probably involving a carbocationic intermediate. The same mechanistic interpretation was given most reasonably for the nucleophilic participation in the solvolysis of 1-arylethyl chlorides deactivated by strongly electron attracting ring substituents.12) The p-Me derivative of 3 has also been found to be correlated with an m value of >0.98 and a small but still significant l value of 0.3.13) The m value of essentially unity appears to preclude the involvement of nucleophile during ionization, favoring the two step mechanism. The α-cyano group in 3 exerts only insignificant deactivating effect on the ionization while significant enhancement for nucleophilic solvent attack on the intermediate. Further studies are now in progress to establish the detailed solvolytic mechanism in the relevant deactivated systems and the result will be reported in subsequent papers.

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