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The γ-silicon effect on solvolyses of the 3-(aryldimethylsilyl)propyl system

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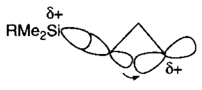
ABSTRACT: The γ-silicon effects in solvolyses were studied mechanistically on 3-(aryldimethylsilyl)propyl tosylates in various solvents based on the substituent effects. The mechanism can be described as competing reactions of the γ-silyl-assisted (k_{Si}) and the solvent-assisted (k_{s}) pathways. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: γ-silicon effect; γ-silyl-assisted solvolysis; percaudal interaction; substituent effect; Yukawa–Tsuno equation; solvent effect

INTRODUCTION

The solvolysis of propyl sulfonates is greatly accelerated by γ-silyl substituents, especially when the Si—C$_{\gamma}$ bond and the C—O bond of the leaving group are disposed in a planar W conformation. The so-called γ-silicon effect is due to the interaction of the back lobe of the Si—C$_{\gamma}$ bond with the developing vacant p-orbital on the cationic center (percaudal interaction) (**1**).[1,2] A free rotating primary system, in which the W conformation between the γ-silyl group and the leaving groups is unrestricted owing to the flexible Si—C—C—C—Lv chain, has never been studied in detail.[2]

We recently reported that the γ-silyl-assisted (k_{Si}) solvolyses of 3-(aryldimethylsilyl)-2,2-dimethylpropyl sulfonates (**3**) exhibited large rate accelerations (10^3–10^4)-fold due to the formation of the γ-silyl-stabilized carbocation **1** with concomitant migration of the (ArMe$_2$Si)methyl group. Solvent effects according to the Winstein–Grunwald equation[3] were found to be similar to those observed for the k_{Δ} solvolyses of various β-arylalkyl systems.[4] However, assistance by the Si—C$_{\gamma}$ bond was less than half that obtained for *p*-MeO-neophyl solvolysis where the positive charge is strongly delocalized into a bridged phenonium ion (**2**, X = *p*-MeO). The effects of aryl substituents on the silyl atom on the solvolyses of **3** were correlated with unenhanced $\sigma°$ parameters, giving ρ values of ca -1.0.[5] These results demonstrated that a certain extent of positive charge exists on the γ-silicon atom, reflecting the delocalization of incipient carbocationic charge by participation of the Si—C$_{\gamma}$ bond. All these results were in line with the rate-determining formation of the bridged transition state **1** stabilized by the γ-silyl group.



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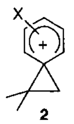

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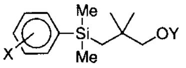

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In order to substantiate the γ-silicon effect in a primary system, we undertook detailed studies of the solvolysis mechanism of 3-(aryldimethylsilyl)propyl tosylates (**4**). In this paper, the solvolysis of **4** is discussed based on the effects of substituents and solvents, in comparison with the γ-silyl-assisted solvolysis of the 3-(aryldimethylsilyl)-2,2-dimethylpropyl system (**3**).

RESULTS AND DISCUSSION

The solvolysis rates of **4** with various ring substituents were determined conductimetrically in 60% (v/v) aqueous ethanol (60E) and 70% (w/w) aqueous 2,2,2-trifluoroethanol (70T) at 70 °C and 97% (w/w) aqueous 2,2,2-trifluoroethanol (97T) at 75 °C.[6]

The H derivative of **4** solvolyzes slightly slower than the non-silylated derivative, propyl tosylate ($k = 6.804 \times 10^{-5}$ s^{-1}) in 60E at 70 °C; on the other hand, it solvolyzes 3.4 times faster than the propyl tosylate ($k = 1.231 \times 10^{-5}$ s^{-1}) in 70T at 70 °C. The rate change with ring substiuents was fairly small but varied with the solvent; only 1.2-fold in highly nucleophilic 60E, but 4-fold in the less nucleophilic solvent 70T and 7-fold in the much less nucleophilic solvent 97T for a wide range of substituent changes from the *p*-MeO to *m*-CF$_3$ (Table 1).

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Table 1. Rate constants for solvolyses of 3-(aryldimethylsilyl)propyl tosylates (**4**)[a]

	$10^5k(s^{-1})$		
Substituent	60E[b] at 70 °C	70T[c] at 70 °C	97T[d] at 75 °C
p-MeO	6.27	5.85	4.30
p-Me	6.02	5.95	5.19
m-Me	5.80	5.17	4.29
H	5.75	4.20	3.32
m-Cl-*p*-MeO	5.68	2.91	1.69
p-Cl	5.79	2.52	1.55
m-CF_3	5.20	1.48	0.745

[a] The experimental errors in the respective runs were generally $<1.0\%$ and the reproducibility of the rate constants was within $\pm 1.0\%$.
[b] 60% (v/v) aqueous ethanol.
[c] 70% (w/w) aqueous 2,2,2-trifluoroethanol.
[d] 97% (w/w) aqueous 2,2,2-trifluoroethanol.

These results apparently indicate a mechanistic transition with solvent nucleophilicity.

The solvent effect on this system at 45 °C[6] clearly showed the nucleophilic assistance of the solvent but failed to correlate linearly with the extended Winstein–Grunwald equation ($mY_{OTs} + lN_{OTs}$),[3] providing evidence that the reaction does not proceed either through the formation of a cation intermediate or through an S_N2 mechanism. This suggests that the reaction takes place with competition between γ-silyl-assisted (k_{Si}) and solvent-assisted (k_s) pathways, and the ratio varies with the solvent and with the aryl substituent.

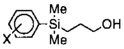
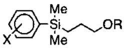
Product analysis

Product analyses for the present solvolyses were carried out in mixed solvents of D_2O and deuterated organic components, such as 60E, ethanol (100E), 70T and 97T in the presence of excess 2,6-lutidine at 75 °C, and quantitatively by using ^{1}H NMR spectroscopy. The products from these solvolyses were found to be exclusively the substitution products and cyclopropane, as summarized in Table 2.

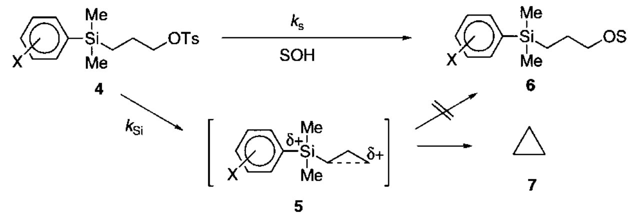
The major products were substitution products in 60E for all substrates accompanied by a small amount (4–16%) of cyclopropane; the latter slightly increased with the electron-donating aryl substituents. In 100E, a slightly more nucleophilic and less ionizing solvent than 60E, the substitution product (the ethyl ether) was obtained exclusively for all derivatives without cyclopropane ($\leq 1\%$). On the other hand, in a less nucleophilic and highly ionizing solvent, 70T, the major product was cyclopropane (53–84%) accompanied by a minor amount of substitution products. In 97T, a further less nucleophilic solvent, cyclopropane was formed exclusively ($\geq 94\%$).

Cyclopropane should be exclusively formed by 1,3-elimination from the carbocation stabilized by the γ-silyl group; therefore, the present solvolysis of **4** proceeds exclusively via the γ-silyl-assisted pathway in 97T. We carried out the product analysis of the α-d_2-labeled **4**. The products in the solvolyses of *p*-MeO, H and *m*-CF_3 derivatives of α-d_2-labeled **4** appear to be essentially the

Table 2. Products (%) for solvolyses of **4** at 75 °C[a]

Solvent[b]	Substituent			Cyclopropane[c]
100E	*p*-MeO	—	99	1
	H	—	>99	<1
	m-CF_3	—	100	0
60E	*p*-MeO	46	38	16 (14)
	p-Me	48	39	13
	m-Me	48	40	12
	H	49	40	11 (8)
	m-Cl-*p*-MeO	52	41	7
	p-Cl	53	41	6
	m-CF_3	52	44	4 (2)
70T	*p*-MeO	16	0	84 (83)
	p-Me	16	0	84
	m-Me	17	0	83
	H	21	0	79 (77)
	m-Cl-*p*-MeO	28	0	72
	p-Cl	31	0	69
	m-CF_3	46	1	53 (51)
97T	*p*-MeO	0	0	100
	H	<1	>1	98
	m-CF_3	2	4	94

[a] Products, given as percentages, were determined by ^{1}H NMR *in situ*. All reactions were carried out in the presence of 2,6-lutidine in deuterated solvents up to completion.
[b] See footnotes b–d in Table 1.
[c] Values in the parentheses were obtained for the solvolyses of α-d_2-labeled substrates.



Scheme 1

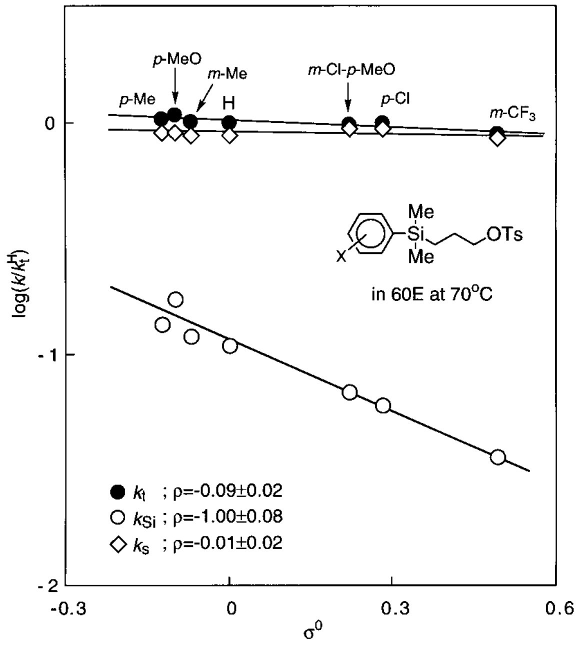


Figure 1. $\sigma°$ plots for the solvolysis of 3-(aryldimethylsilyl)-propyl tosylates (**4**) in 60% (v/v) aqueous ethanol at 70 °C. (●) k_t; (○) k_{Si}; (◊) k_s

same as those for undeuterated substrates in 60E and 70T, as shown in parentheses in Table 2. It is an important finding that no d_2-scrambled tosylates, alcohols or ethers, which would arise as a result of the internal return or the substitution with solvent(s) in the bridged intermediate, were observed in both solvents. As a conclusion, the γ-silyl-assisted pathway does not give the substitution products but exclusively cyclopropane, and furthermore any substitution products should arise from the solvent-assisted pathway, as depicted in Scheme 1.

While the solvent-assisted pathway might be preferred to the γ-silyl-assisted pathway, for the solvolysis of **4** in a highly nucleophilic solvent such as the aqueous ethanol, the latter pathway appears to be enhanced slightly with an increase in the water content. On the other hand, in a less nucleophilic and highly ionizing solvent such as the aqueous 2,2,2-trifluoroethanol (TFE) series, the solvolysis of **4** occurs preferentially through the γ-silyl-assisted pathway, whereas in more aqueous TFE solvents the reaction proceeds to an increased extent through the solvent-assisted pathway. In each solvent, an electron-donating aryl substituent on the silicon atom increases the yield of cyclopropane due to the facile formation of the cation stabilized by a γ-silyl group.

Substituent effect

The Yukawa–Tsuno (Y–T) equation [Eqn. (1)] is one of the most useful tools for predicting the characteristics of the transition state whose reaction center is affected by the benzene π-system:[7]

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

where $\sigma°$ is the normal substituent constant, which involves no additional π-electronic interaction between the substituent and reaction center, $\Delta\bar{\sigma}_R^+$ is the resonance substituent constant measuring the capability for π-delocalization of a p-π-electron-donor substituent, defined by $\sigma^+ - \sigma°$, and r is a parameter characteristic of a given reaction, measuring the degree of resonance interaction between the aryl group and the reaction site in the rate-determining step.

The logarithms of the relative rates in 97T at 75 °C were correlated directly with $\sigma°$ (i.e. $r = -0.03 \pm 0.02$), giving a ρ value of -1.32. This small but negative ρ value suggests that a significant amount of positive charge resides on the Si atom at the γ-position. The zero r value assigned for this system may be explicable if the phenyl π-system on the γ-silicon atom interacts through the Si—C σ-bond only indirectly (by a non-π-interaction mechanism) with the carbocationic reaction center in **5**. The magnitude of the substituent effect obtained in 97T is similar to that ($\rho = -1.10$ and $r = -0.03$) for the γ-silyl-assisted solvolysis of 3-(aryldimethylsilyl)-2,2-dimethylpropyl brosylate (**3**) in 97T.[5]

Substituent effects for the solvolysis of **4** in 60E at 70 °C are plotted against $\sigma°$ in Fig. 1 and the essentially zero susceptibility ($\rho = -0.09$) plausibly means that the solvolysis predominantly proceeds in 60E via the solvent-assisted mechanism. This is substantiated by the major yield (96–84%) of substitution products for all substituents. On the other hand, as shown in Fig. 2, the analysis for the solvolysis of **4** in 70T gave $\rho = -0.95 \pm 0.04$ with $\sigma°$ ($R = 0.997$ and $SD = \pm 0.02$) which are close to those for **4** in 97T and **3**. This demonstrates that the solvolysis of **4** in 70T proceeds mainly through the γ-silyl-assisted carbocation **5**. In fact, the product analysis shows a major yield (53–84%) of cyclopropane for all substituents.

However, for the solvolysis of **4** in either 60E or 70T, the apparent rate constants, k_t, are expressed by the sum of the rate constants for γ-silyl-assisted (k_{Si}) and solvent-assisted (k_s) pathways: $k_t = k_{Si} + k_s$. The overall rate constants k_t should be divided into the composite rate

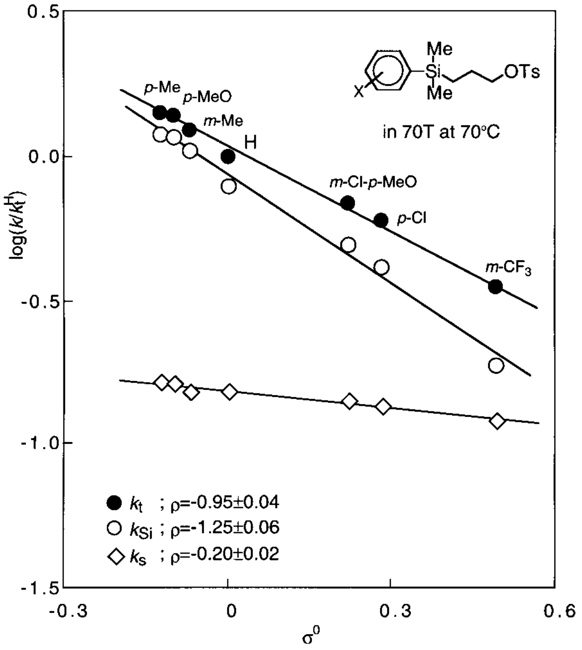


Figure 2. $\sigma°$ plots for the solvolysis of 3-(aryldimethylsilyl)-propyl tosylates (**4**) in 70% (w/w) aqueous 2,2,2-trifluoroethanol at 70°C. (●) k_t; (○) k_{Si}; (◊) k_s

constants k_{Si} and k_s in order to analyze the mechanism quantitatively. Assuming the products to be entirely kinetically controlled, k_{Si} and k_s are represented by $k_{Si} = k_t P_{Si} / (P_{Si} + P_s)$ and $k_s = k_t P_s / (P_{Si} + P_s)$, where P_{Si} and P_s are the product percentage ratios for the γ-silyl-assisted (k_{Si}) and the solvent-assisted (k_s) pathways, respectively. As cyclopropane and substitution products were derived from the γ-silyl-assisted mechanism and the S_N2 displacement, respectively, P_{Si} and P_s can be calculated from the amounts of cyclopropane and substitution products, respectively, in Table 2. Hence the overall k_t in Table 1 could be dissected into the partial rate constants k_{Si} and k_s by using product ratios.

The substituent effects on the solvolyses of **4** in 60E and 70T are displayed clearly in Figs 1 and 2, respectively, where the logarithms of k_t, k_{Si} and k_s are plotted against $\sigma°$. The linear $\sigma°$ relationships indicate that the k_{Si} and k_s pathways should proceed by mechanisms free from the significant π-delocalization interaction of the p-π-electron-donor substituent.

The effects of aryl substituents on the γ-silyl atom on the k_{Si} pathway gave ρ values of -1.0 in 60E and -1.25 in 70T with a $\sigma°$ parameter, reflecting the delocalization of incipient carbocationic charge by participation of the Si—C$_\gamma$ bond in **5**. These ρ values for the k_{Si} pathway were fairly close to those for the solvolyses of **4** in 97T and 3-(aryldimethylsilyl)-2,2-dimethylpropyl brosylate (**3**) in 60E ($\rho = -0.87$) and 97T ($\rho = -1.08$).[5] In each solvent, the k_{Si} correlation against the $\sigma°$ scale with a small ρ value is consistent with the structure of the Si—C$_\gamma$ bridged transition state **1** or **5**.

The substituent effect on the partial rates for the k_s pathway was characterized by negligibly small ρ values of -0.01 ± 0.02 in 60E and -0.20 ± 0.02 in 70T against $\sigma°$. These k_s correlations of essentially zero susceptibility with the aryl substituents on the γ-silicon atom are compatible with those for a concerted S_N2 displacement mechanism at the remote reaction center with no significant cationic charge.

In conclusion, the solvolysis of **4** can be described as competing reactions of the γ-silyl-assisted (k_{Si}) and the solvent-assisted (k_s) pathways, as outlined in Scheme 1. The ratio of these two pathways depends on the solvolyzing solvents and the X-phenyl substituents on the γ-silicon atom.

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