

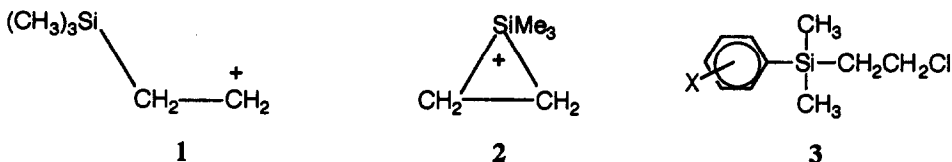
Substituent Effect on Solvolysis of 2-(Aryldimethylsilyl)ethyl Chlorides

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Abstract: The solvolysis rates of 2-(aryldimethylsilyl)ethyl chlorides **3** were measured using a conductometric method. The analysis of the Yukawa-Tsuno LArSR equation gives a reaction constant of $\rho = -1.42$ and a high resonance demand of $r = 1.48$. This result indicates that the β -silicon effect is attributed to the cyclic transition state structure with a positive charge on the silicon in this primary system.

It is well known that a trimethylsilyl group strongly stabilizes a carbocation at the β position (so-called β -silicon effect).¹⁾ The studies of this effect have recently been experimentally and theoretically carried out.²⁾ Many chemists are explaining the β -silicon effect by Si-C hyperconjugation **1** or cyclic structure **2**.¹⁻³⁾



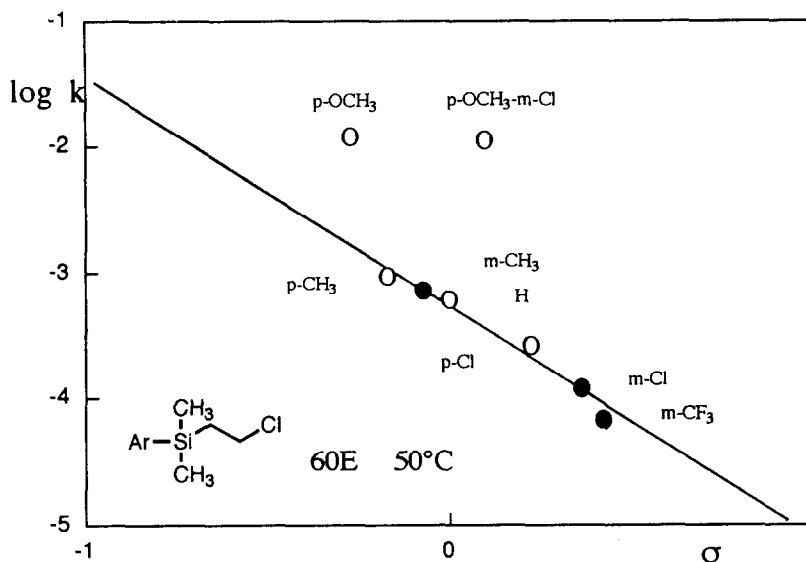
The differences in these two structures are the position of the positive charge and the distance between the silicon group and carbocation site. For the position of positive charge, it should be possible to examine it by the substituent effect of an aryl group on the silicon. Because the substituent effect changes with the position of charge and the distance between the reaction site and aryl group. From this viewpoint, Vencel et al. have already reported the substituent and solvent effects on the solvolysis of 1-(aryldimethylsilyl)ethyl chlorides **3**.⁴⁾ However, they could not analyze the substituent effect with strongly electron-donating substituents. Therefore, in order to clarify the stabilization mechanism (transition state structure), we measured the solvolysis rates of 1-(aryldimethylsilyl)ethyl chlorides **3**, including strongly electron donating *p*-OCH₃ and *p*-OCH₃-*m*-Cl substituents, and analyzed the substituent effect of aryl group on the silicon atom.

2-(Aryldimethylsilyl)ethyl chlorides **3** were synthesized by the procedures of Vencel et al.⁴⁾ The solvolysis rates of *p*-OCH₃ and *p*-OCH₃-*m*-Cl derivatives were immediately measured after vacuum distillation, because both derivatives decomposed at room temperature. The solvolysis rates were conductometrically measured in various aqueous solvents at 50°C.⁵⁾ The solvolysis followed a first-order reaction rate law until 4 half-lives. These rate constants are summarized in Table 1. Vencel et al. have reported the deviations from the first-order

Table 1. Rate constants of Solvolysis for 2-(Aryldimethylsilyl)ethyl Chlorides at 50 °C

Substituent	Solvent ^a	$10^4 k(\text{s}^{-1})$	Substituent	Solvent	$10^4 k(\text{s}^{-1})$
p-OCH ₃	60E	118.5	p-Cl	60E	2.591
p-OCH ₃ -m-Cl	60E	109.9 ^b	m-Cl	60E	1.177
p-CH ₃	60E	9.484	m-CF ₃	40E	5.322
3,5-(CH ₃) ₂	60E	7.921		50E	2.065
m-CH ₃	60E	7.186		60E	0.7098
H	40E	47.04		70E	0.2722
	50E	16.27		80E	0.0854
	60E	5.950		50A	1.134
	70E	2.053		60A	0.2901
	80E	0.6062		70A	0.8047
	50A	9.073		50T	13.39
	60A	2.296		97T	3.399
	70A	0.572			
	50T	127.3			
	97T	48.12			

^a 40E-80E: 40/60-80/20(v/v) ethanol/water; 50A-70A: 50/50-70/30(v/v) acetone/water; 50T-97T: 50/50-97/3(w/w) trifluoroethanol/water mixtures. ^b Average of duplicate runs.

Fig. 1. The σ plot for solvolysis of 2-(aryldimethylsilyl)ethyl chlorides.

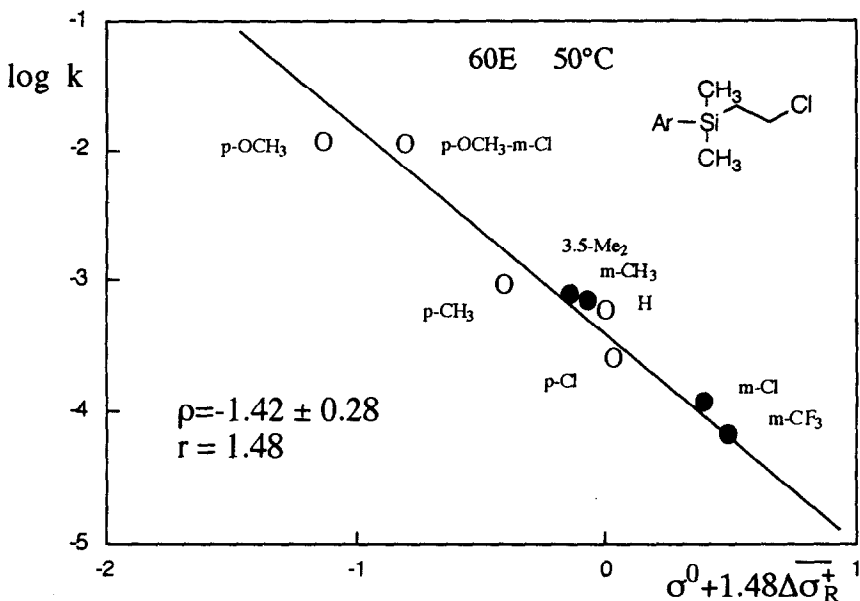


Fig. 2. The LArSR plot for solvolysis of 2-(aryldimethylsilyl)ethyl Chlorides.

dependence in the acid-catalyzed solvolysis of (2-hydroxyethyl)*p*-anisyl(dimethyl)silane and (2-hydroxyethyl)*p*-tolyl(dimethyl)silane and the easy dearylation for electron-donating substituents.^{4,6} The dearylation leads to the decrease of solvolysis rate because of the formation of the less reactive disiloxane.⁶ These reactions seem not to be important in the present solvolysis, because the solvolysis rate of the *p*-OCH₃-*m*-Cl substituent decelerated slightly in the presence of 2,6-lutidine⁷) and because the *p*-OCH₃ and *p*-OCH₃-*m*-Cl derivatives are more reactive than the other derivatives. The Hammett plots are shown in Figures 1 and 2. From the *m*-CF₃ substituent to the *p*-CH₃ one, the rate constants are correlated with the Hammett σ substituent constants, as the result of Vencel. However, strongly electron-donating substituents (*p*-OCH₃ and *p*-OCH₃-*m*-Cl substituents) were deviated in the direction of activation from the correlation line. In contrast, in the LArSR plot the rate constants of all substituents is well correlated. The reaction constant ρ value is -1.42 and the r value, which is a parameter of the resonance demand, is 1.48.⁸) It is very important that the r value is larger than unity, since the r value implies the degree of resonance interaction between the aryl group and the reaction site in the rate-determining transition state. Even in the solvolysis of 1,1-dimethylbenzyl chloride which proceeds through a stable benzylic carbocation intermediate, the r value is unity.⁹) These results indicate that the positive charge locates on the silicon atom in the transition state and that the silicon atom possesses a similar ability to delocalize the positive charge onto the aromatic system like a carbon atom. Generally, the reaction that gives a large r value shows a large ρ value.¹⁰) The reaction constant ρ value of the present solvolysis appears to be small when compared with the r value. Mishima and Tsuno have reported that the ρ value of the solvolysis is smaller than that of the gas phase because of the dispersion of the positive charge by solvation.¹¹) On the basis of this fact and the availability of empty 3d orbitals of silicon, we imagine that a large dispersion of the positive charge on the silicon may cause the small ρ value. Actually, the ρ value of the substitution reaction on the silicon atom is

small.¹²⁾ To discuss the β -silicon effect in more detail, the substituent effects of aryl group at silicon atom on the solvolysis of other β -silicon derivatives are now being performed.

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References and Notes

- For example, see: J.B. Lambert, *Tetrahedron*, **1990**, *46*, 2677 and references cited therein.
- (a) J.B. Lambert, G.-T. Wang, R.B. Finzel, and D.H. Teramura, *J. Am. Chem. Soc.*, **1987**, *109*, 7838. (b) N. Shimizu, S. Watanabe, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **1991**, *64*, 2249. (c) M.R. Ibrahim and W.L. Jorgensen, *J. Am. Chem. Soc.*, **1989**, *111*, 819.
- M.A. Cook, C. Earbon, and D.R.M. Walton, *J. Organometal. Chem.*, **1970**, *24*, 301.
- J. Vencel, K.J. Hetflejs, J. Cermak and V. Chvalovsky, *Collect. Czech. Chem. Commun.*, **1973**, *38*, 1256.
- Vencel et al. followed the volume of ethylene evolved with time. They have not reported the observed rate constants of 1-(aryldimethylsilyl)ethyl chlorides **3**. Therefore, in order to confirm their analyzed results, we also studied the solvent effects on the solvolysis of 2-(phenyldimethylsilyl)ethyl and 2-(m-trifluoromethylphenyldimethylsilyl)ethyl chlorides. Both derivatives showed a single linear response to the solvent ionizing power Y of aqueous ethanol, acetone, and 2,2,2-trifluoroethanol (TFE). The m values, which is the sensitivity to solvent ionizing power Y , were 0.73 and 0.67 for unsubstituted and m -CF₃ derivatives, respectively. These m values are slightly smaller than those of Vencel's results.
- J. Vencel, K.J. Hetflejs, P. Kucera, J. Cermak, and V. Chvalovsky, *Collect. Czech. Chem. Commun.*, **1973**, *38*, 1248.
- The solvolysis rate constant for the p -OCH₃- m -Cl substituent is 9.66×10^{-3} in the presence of 2,6-lutidine (6 equivalent mole).
- The reaction constant and r values are -1.62 and 1.03, respectively, except for p -OCH₃- m -Cl derivative. The r value strongly depends on the substituents set. But the r value is at least larger than unity.
- H.C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **1957**, *79*, 1911.
- A. Murata, S. Sakaguchi, R. Fujiyama, M. Mishima, M. Fujio, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **1990**, *63*, 1138.
- (a) M. Mishima, H. Inoue, M. Fujio, and Y. Tsuno, *Tetrahedron Lett.*, **1989**, *30*, 2101. (b) Y. Tsuno, A. Murata, M. Goto, and M. Fujio, "Physical Organic Chemistry 1986," ed. by M. Kobayashi, Elsevier, Amsterdam 1987, pp. 167.
- The solvolysis rates of arylchlorodimethylsilanes in aqueous dioxane were analyzed based on the σ^0 substituent constants. The reaction constant ρ value is about 1.2. (N. Takeshue, T. Tsutsumi, N. Shimizu, and Y. Tsuno, 63rd National Meeting of the Chemical Society of Japan, Osaka, March 1992, Abstr. No. 2B317.)

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