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A Quantitative Scale for the Structural Effect on Reactivity toward Nucleophilic Displacement at Silicon

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The rates of solvolysis for forty different triorganochlorosilanes have been measured in 89 mol% aqueous dioxane at 25 °C; the logarithmic rates relative to that for trimethylchlorosilane, $\log k_{rel} = \log [k(R^1R^2R^3SiCl) / k(Me_3SiCl)]$, provide a quantitative scale for the structural effect of various silyl groups on the reactivity toward nucleophilic displacement at silicon, ranging from 1.99 for $HSiMe_2$ to -6.89 for *t*-$BuSiPh_2$ groups.

Various silyl groups are used in organic synthesis as a protecting group[1)] or as a key substituent capable of inducing unique stereo- and regioselectivities; however, quantitative scales for the structural effect of a wide variety of silyl groups on the reactivity towards nucleophilic displacement at silicon are not available at present.[2)]

In order to make such a scale we selected the solvolysis of triorganochlorosilanes. Simple trialkylchlorosilanes are often too reactive to measure the rates of solvolysis by the usual techniques.[3)] We have found that most triorganochlorosilanes solvolyze in aqueous dioxane containing 2–20 mol% water at convenient rates for the stopped-flow spectrophotometric technique. Table 1 summarizes the results of solvolysis for forty different triorganochlorosilanes in a 11/89 (mol%) water/dioxane mixture (abbreviated as 89D) at 25 °C; the rates relative to that for trimethylsilyl chloride ($k = 126.1 \pm 1.1\ s^{-1}$) are given as the logarithmic values, $\log k_{rel}$.

$$R^1R^2R^3SiCl \xrightarrow[\text{acridine}]{\text{aq. dioxane}} R^1R^2R^3SiOH + \text{acridinium chloride}$$

The solvolysis was followed by a Photal RA-401 stopped-flow spectrophotometer (Otsuka Electronics), and was initiated by mixing the same volumes of the two stock solutions, one being a 4.0×10^{-4} mol dm^{-3} solution of a given chlorosilane in dioxane and the other being an 8.0×10^{-4} mol dm^{-3} solution of acridine (as an acid quencher) in a 1.00/20.0 (v/v) water/dioxane mixture; the resulting solution corresponds to 89 D. The increase in hydrogen chloride produced was monitored as the acridinium salt at 402.5 nm.[4,5)] The solvolysis followed excellent first-order kinetics (correlation coefficient $R > 0.9999$ using more than 80 data points measured during the first 3 half-lives), and at least duplicate determinations of the rates were made for each substrate; the rates were reproducible within an accuracy of ±4%. The solvolysis for the substrates which are either more reactive than (*p*-nitrophenyl)dimethylchlorosilane or less reactive than *t*-butyldimethylchlorosilane was too rapid or too slow to measure the rates in 89D; so, the rates for the former substrates were determined in less aqueous media, 98D or 95D, while those for the latter, in a more aqueous solvent 82D. The rates determined in these solvents were extrapolated to the solvolysis rates in 89D.[6)] The rate of solvolysis of *t*-$BuSiPh_2Cl$, which was the least reactive

Table 1. Relative Rates of Solvolysis for Various Triorganochlorosilanes in 89 mol% Aqueous Dioxane at 25.0±0.05 °C [a]

Run	Silyl group	log k_{rel}	Run	Silyl group	log k_{rel}
1	$HSiMe_2$	1.990 [b]	21	t-$BuCH_2OSiMe_2$	-0.893
2	$Cl_2CHSiMe_2$	0.896 [c]	22	p-$CH_3C_6H_4SiMe_2$	-0.925
3	$CF_3CH_2OSiMe_2$	0.759 [c]	23	$Me_3SiCH_2SiMe_2$	-1.032
4	$ClCH_2SiMe_2$	0.540 [c]	24	t-$BuCH_2SiMe_2$	-1.237
5	$[MeO(CH_2)_2O]SiMe_2$	0.281 [c]	25	i-$PrSiMe_2$	-1.421
6	p-$NO_2C_6H_4SiMe_2$	0.0935	26	s-$BuSiMe_2$	-1.478
7	$NC(CH_2)_3SiMe_2$	0.0671	27	$(n$-$Bu)_2SiMe$	-1.560
8	Me_3Si	(0.0) [a]	28	c-$C_6H_{11}SiMe_2$	-1.589
9	$MeOSiMe_2$	-0.342	29	t-$BuOSiMe_2$	-1.628
10	$[MeO(CH_2)_3]SiMe_2$	-0.359	30	EtO_3Si	-1.695
11	$EtSiMe_2$	-0.547	31	$Et_2CHSiMe_2$	-1.714
12	$EtOSiMe_2$	-0.559	32	Et_3Si	-1.869
13	$C_6H_5CH_2SiMe_2$	-0.560	33	$(C_6H_5)_2SiMe$	-2.157
14	n-$PrSiMe_2$	-0.662	34	$(n$-$Bu)_3Si$	-2.567
15	i-$PrOSiMe_2$	-0.703	35	$MeSi(i$-$Pr)_2$	-3.066
16	n-$BuSiMe_2$	-0.730	36	$(C_6H_5)_3Si$	-3.438
17	$Me_3SiSiMe_2$	-0.743	37	t-$BuSiMe_2$	-3.507
18	i-$BuSiMe_2$	-0.840	38	i-$PrCMe_2SiMe_2$	-3.988 [e]
19	$C_6H_5SiMe_2$	-0.851	39	$(i$-$Pr)_3Si$	-4.968 [e]
20	n-$C_{18}H_{37}SiMe_2$	-0.860	40	t-$BuSi(C_6H_5)_2$	-6.893 [f]

a) Relative to the rate for trimethylchlorosilane: k = 126.1±1.1 s^{-1}. b) Calculated from a $k(HSiMe_2Cl)$ / $k(Me_3SiCl)$ ratio of 97.7 in 98D. c) Extrapolated from the rates in 95D. e) Extrapolated from the rates in 82D. f) Determined by the usual spectrophotometric method (Ref. 4)

substrate examined in the present work, was measured by the usual spectrophotometric method.[4] A comprehensive set of the log k_{rel} values listed in Table 1 provides a precise and useful scale for the structural effect of triorganosilyl groups on the reactivity toward nucleophilic reactions at silicon. The scale ranges from 1.99 for $HSiMe_2$ to -6.89 for t-$BuSiPh_2$ covering reactivities of 10^9 in rate.

The structural effect of silyl groups certainly involves electronic and steric factors.[7] Figure 1 shows a plot of log k_{rel} against the revised Taft steric parameter E_s' [8] for a series of R-substituted dimethylchlorosilanes, $RSiMe_2Cl$ (Methyl was taken as a reference standard). Several features are worthy of note. First, a linear relationship expressed as Eq. 1 is noticed for alkyl groups including Me, Et, n-Pr, n-Bu, i-Pr, c-C_6H_{11}, t-Bu, and

$$\log k_{rel} = 2.1\,E_s' - 0.22 \quad (n = 8, R = 0.991) \qquad (1)$$

also hydrogen, indicating that the structural effect of alkyl substituents is steric in origin. There are, however, several alkyl groups that markedly deviate from the correlation line; they include *s*-Bu, *i*-Bu, neopentyl, Et_2CH, and *i*-$PrCMe_2$. Since there is little difference in the electronic effect among the alkyl groups,[9] the deviation should be ascribed to the difference between the steric effect at silicon and that at carbon. Apparently, a new set of the steric constants is needed for the analysis of the reactions at silicon. The present "log k_{rel}" values for the alkyl groups serve as a quantitative scale for the steric effect involved in the reactions at silicon. In order to discuss the steric effect at silicon on the same Taft scale, we define a new set of the steric constants termed E_s^{Si} by dividing the log k_{rel} values by the sensitivity of 2.1 to E_s', i.e., $E_s^{Si} = (\log k_{rel}) / 2.1$.

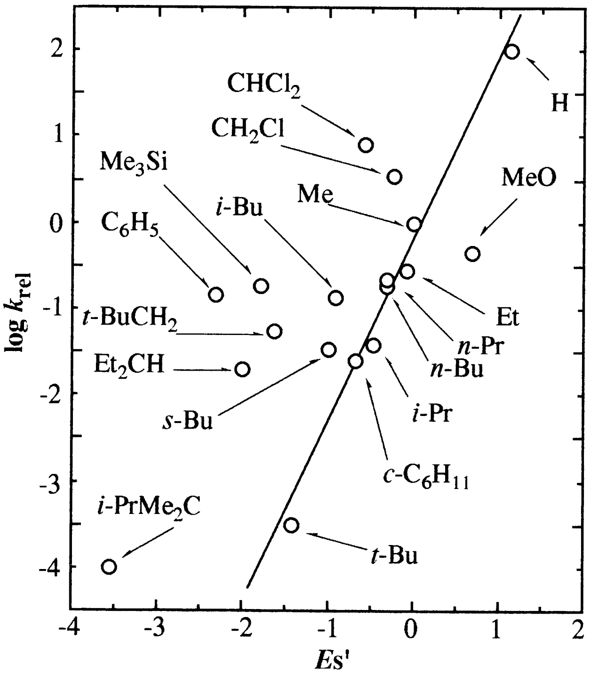

Fig.1. A plot of log k_{rel} for $RSiMe_2Cl$ vs. *E*s'.

Table 2. Steric Constant E_s^{Si}

R	$-E_s^{Si}$	$-E_s'$ a)
H	-0.948	-1.12
Me	0	0
Et	0.261	0.08
n-Pr	0.315	0.31
n-Bu	0.348	0.31
i-Bu	0.400	0.93
neopentyl	0.589	1.63
i-Pr	0.677	0.48
s-Bu	0.704	1.00
c-C_6H_{11}	0.757	0.69
Et_2CH	0.816	2.00
t-Bu	1.670	1.43
i-$PrCMe_2$	1.899	3.54

a) Ref. 8.

Table 2 shows a comparison between the E_s^{Si} and E_s' values for various alkyl groups. Interestingly, the E_s^{Si} values are roughly in the order, primary > secondary > tertiary alkyls, rather than in the order of steric bulk expressed by the Taft steric parameter. Thus, the difference in E_s^{Si} between *n*-Bu and neopentyl, between *i*-Pr and Et_2CH, or between *t*-Bu and *i*-$PrCMe_2$, is much smaller than that in E_s' in each case. The solvolysis of the chlorosilanes listed in Table 1 probably proceeds via a five-coordinate intermediate species;[10] the conformational situation of the alkyl groups, $R^1R^2R^3C$, in the transition state of the nucleophilic displacement at silicon seems considerably different from that in the transition state of the S_N2 reactions at carbon.

Figure 1 also shows deviation from Eq. 1 for phenyl, CH_2Cl, $CHCl_2$, $SiMe_3$, and MeO groups. The deviation for these groups is probably associated with the electronic effect; however, since these groups may have the E_s^{Si} values significantly different from E_s', the structural effect of these groups should be discussed in detail after the steric effect of these groups on the reactivity at silicon is established.

Finally, it is instructive to note that the steric effect of alkyl groups around silicon is approximately (but not exactly) additive, as indicated by the regular change of the log k_{rel} values in the series $RSiMe_2Cl$, $R_2SiMeCl$, and R_3SiCl (R = Et, *n*-Bu, and *i*-Pr) in the ratio 1:2.2:3.5.

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5) The effect of acridine on the rate of solvolysis was checked using $PhSiMe_2Cl$; the rates of solvolysis in 89.4D did not vary with acridine concentration in a range of (2-10) x 10^{-4} mol dm^{-3}, indicating unimportance of the base catalysis by acridine, although the base catalysis was in fact involved in the solvolysis in much less aqueous media such as 99.5D.
6) The extrapolation was made on the basis of the following linear relationships between the rates of solvolysis in 89D and those in 95D or 82D:

$$\log k^{89D} = \log k^{95D} + 1.439 \quad (n = 10, R = 0.998)$$

and

$$\log k^{89D} = 0.870 \log k^{82D} - 1.129 \quad (n = 5, R = 0.998).$$

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