SHORT COMMUNICATION

The potentiometric titration of siloxane structures with n-Bu₄NOH titrant

It is a well known fact that the Si–O–Si bonds are readily cleaved by strong nucleophilic reagents[1]. The technologically important base-catalyzed polymerization of cyclic siloxanes to high polymers presumably goes through such a mechanism[2]. The influence of substituents attached to the silicon atoms upon this reaction is less well understood.

We have now found that we can titrate hexaorganocyclotrisiloxanes and some other siloxane materials as very weak acids with tetra-n-butylammonium hydroxide titrant in pyridine. The system employed is one similar to that described for the titration of phenols[3] or silanols[4].

Experimental

The siloxanes employed in this study were research materials from Dow Corning Corporation Laboratories and were previously characterized by conventional
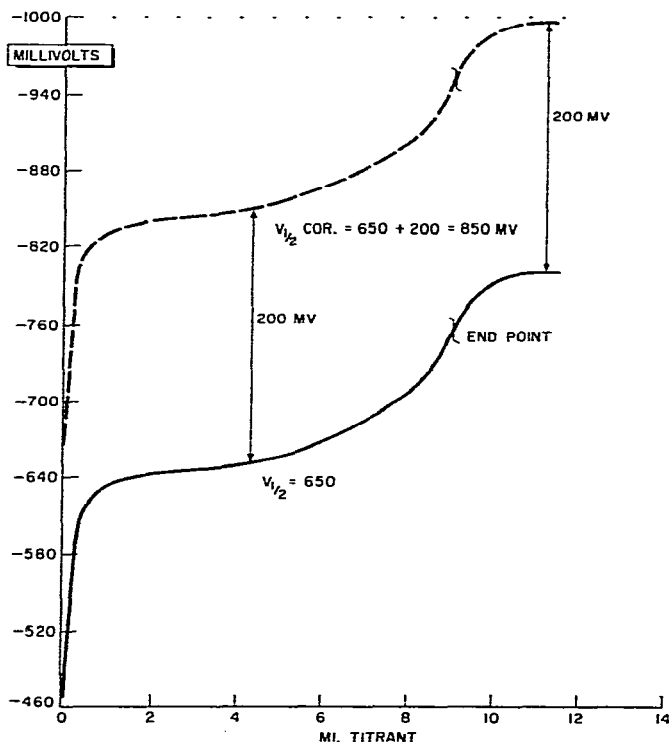

Fig. 1. Typical titration of 2,2,5,5-tetraphenyl-1,2,5-oxadisilolane, $Ph_2SiCH_2CH_2SiPh_2$. The dashed line
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represents the curve obtained by shifting the experimental curve to the arbitrary post end point voltage of -1000 mv.

means. Potentiometric titrations were carried out using a modified* Beckman No. 39142 combination electrode in conjunction with a Beckman model G pH meter. Eastman Organic Chemical's tetrabutylammonium hydroxide titrant (25% in methanol) was diluted with dry benzene to about 0.1 M and standardized against benzoic acid dissolved in pyridine with thymolphthalein as the indicator. Enough of the siloxane samples to require approximately 10 ml of titrant were weighed and dissolved in 40 ml of previously dried pyridine. The samples and titrant were maintained dry and free from carbon dioxide by means of a dry nitrogen atmosphere over the sample and self-leveling closed titration apparatus with reservoir.

TABLE 1

SILOXANE TITRATION DATA

Compound	$-V_{1/2}$(volts)[a]	$\Sigma\sigma^{*}$ [b]	Ratio $\dfrac{trimer\ eqs.\ found}{trimer\ eqs.\ used}$ [c]
[(CF$_3$CH$_2$CH$_2$)$_2$SiO]$_3$	0.80	1.92	1.00, 0.98
[(CF$_3$CH$_2$CH$_2$)$_2$SiO]$_4$	0.81		0.94, 0.96
Ph$_2$SiCH$_2$CH$_2$SiPh$_2$ ⌊—O—⌋	0.85		1.04, 1.03, 1.00, 0.99 0.94, 1.02, 1.02, 1.05
(Ph$_2$SiO)$_4$	0.85		0.98, 0.98, 0.99, 1.09
(CF$_3$CH$_2$CH$_2$ViSiO)$_3$	0.86	1.47	0.98, 1.00, 0.98
[(CF$_3$)$_2$CFCH$_2$CH$_2$MeSiO]$_3$	0.88		1.03, 1.02
(C$_3$F$_7$CH$_2$CH$_2$MeSiO)$_3$	0.88		1.00, 1.02
(CF$_3$CH$_2$CH$_2$MeSiO)$_3$	0.89	0.96	1.00, 1.01, 1.00, 0.99 0.99
(PhMeSiO)$_x$ ($x > 10^3$)	0.89		1.00, 0.97, 1.01
[(Ph$_2$SiO)$_2$(PhMeSiO)]$_1$	0.89	1.15	0.97, 0.96
[H(CF$_2$)$_4$CH$_2$CH$_2$MeSiO]$_3$	0.90		1.07, 1.03
(PhMeSiO)$_4$	0.90		1.02, 0.98
(C$_2$F$_5$CH$_2$CH$_2$MeSiO)$_3$	0.90		1.02, 1.03
(Ph$_2$SiO)$_3$	0.90	1.38	1.00, 1.04
(CF$_3$CH$_2$CH$_2$MeSiO)$_4$	0.90		1.07, 1.03
(CF$_3$CH$_2$CH$_2$MeSiO)$_5$	0.91		1.00, 0.95
(CF$_3$CH$_2$CH$_2$MeSiO)$_x$ ($x > 10^4$)	0.91		1.01, 1.04
Ph$_2$SiCH$_2$CH$_2$SiPhMe[c] ⌊—O—⌋	0.91		1.21, 0.99, 1.08, 1.02
(HCF$_2$CF$_2$CH$_2$CH$_2$MeSiO)$_3$	0.91	0.99	1.04, 1.07
(NCCH$_2$CH$_2$CH$_2$MeSiO)$_{3-4}$	0.91		1.02, 1.10, 0.99
(PhMeSiO)$_3$	0.93	0.69	1.10, 1.11, 1.01
(HCF$_2$CH$_2$CH$_2$MeSiO)$_3$	0.94	0.72	1.03, 0.96
[(Ph$_2$SiO)(PhMeSiO)$_2$]$_1$	0.94	0.92	0.97, 0.96
[(Ph$_2$SiO)$_2$(Me$_2$SiO)]$_1$	0.94	0.92	0.99, 1.02
(MeViSiO)$_3$	0.98	0.51	0.99, 0.92
(Me$_2$SiO)$_3$	0.99	0.00	0.97, 1.00
Me$_2$SiCH$_2$CH$_2$SiMe$_2$ ⌊—O—⌋	No detectable end point		
(Me$_3$SiO)$_4$Si	No detectable end point		
(Me$_2$SiO)$_x$ ($x > 100$)	No detectable end point		

[a] Titration curves shifted to arbitrary post end point voltage $= -1.00$ volts. [b] Ref. 8. [c] Ratio of moles oxadisilolane found to moles used for the oxadisilolanes.

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* The electrolyte was dissolved in dry methanol rather than water.[4]

A typical titration curve for 2,2,5,5-tetraphenyl-1,2,5-oxadisilolane, $Ph_2SiCH_2CH_2SiPh_2$, is shown in Fig. 1.

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Results and discussion

Titration curves characteristic of weak acids were obtained for the titration of the siloxanes. A variety of siloxanes with the structure $(R_2SiO)_x$ (Table 1) titrated according to the following equation:

$$3\,(R_2SiO)_x + x\,Bu_4NOH \rightarrow x\,HO(R_2SiO)_3^- N^+Bu_4 \tag{1}$$

Several oxadisilolanes titrated according to the equation:

$$R_2SiCH_2CH_2SiR_2 + Bu_4NOH \rightarrow HOR_2SiCH_2CH_2SiO^-N^+Bu_4 \tag{2}$$

Table 1 lists the ratio of equivalents of base utilized per cyclic equivalent* employed for several siloxane systems. Table 1 illustrates that eqn. (1) is correct regardless of whether the species titrated was cyclic trimer, higher cyclic or linear polymer.

Attack by the base upon a cyclic siloxane would give a silanolate at one end of the molecule and a silanol on the other end of the siloxane chain. The titration results would be the same whether this species then condensed forming a species, end-blocked on each end with a silanolate anion, or remained unchanged. Examination of one siloxane residue neutralized with one equivalent of base by infrared spectroscopy revealed no SiOMe but a broad infrared band around v 3000 cm^{-1} overlapping with the CH stretching region, indicating possible strongly H-bonded SiOH structures. Reaction of $(Ph_2SiO)_3$ with one equivalent of base followed by reaction with excess trimethylchlorosilane yielded primarily $Me_3SiO(Ph_2SiO)_3SiMe_3$ (via NMR). These data would suggest the absence of the condensation reaction.

That the species produced in the titration is $HO(R_2SiO)_3^- N^+Bu_4$ and not one with more or less than three siloxane units could result from stabilization by strong intramolecular hydrogen bonding.
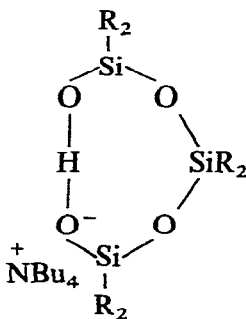
Just as the 8-membered cyclotetrasiloxanes are the most thermodynamically favored with respect to other rings in equilibration of polysiloxanes[5-7] the eight-membered hydrogen bonded ring would also be expected to be favored. Similarly,

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* In this paper cyclic equivalent means: Weight $(R_2SiO)_x$/molecular weight $(R_2SiO)_3$ or weight $(R_2Si\text{-}CH_2CH_2SiR_2O)_x$/molecular weight $R_2SiCH_2CH_2SiR_2$.

the seven-membered ring in the oxadisilolanes would be favored over a fourteen-membered ring, the next larger possible ring.

$$
\begin{array}{c}
\mathrm{CH_2\!\!-\!\!-\!\!-\!\!CH_2} \\
R_2Si \qquad\qquad SiR_2 \\
O\!-\!H\!-\!O^-_+ \\
NBu_4
\end{array}
$$
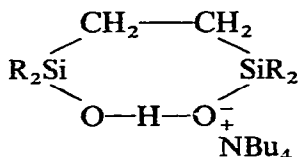
The potential break at the endpoint became sharper with increasing apparent acid strengths. Eight titrations of 2,2,5,5-tetraphenyl-1,2,5-oxadisilolane one of the stronger "acids", were carried out with a standard deviation of 3% in the ratio of equivalents found per equivalent employed.

The relative strength as acids of siloxanes can be determined by comparing their half neutralization voltages. Non-aqueous titrations of this type characteristically give a wide range of half neutralization potentials[8], probably due to variable active surface on the glass electrode. Streuli[8] has overcome this variation by titrating a sample of benzoic acid after each weak acid titration and then comparing the difference in half neutralization potential for the benzoic acid and the weak acid sample. We have found that reliable comparison of relative acid strengths of the siloxanes can be made by adding to the apparent half neutralization voltage, the difference between the post endpoint plateau voltage and some arbitrary voltage (in our case −1000 mv.). That is, the curves are all shifted to an arbitrary constant post endpoint voltage before the half-neutralization voltage is determined. Fig. 1 illustrates this procedure. In this way, adjusted half-neutralization voltages could be determined with a precision of about ±10%. Table 1 lists these adjusted half-neutralization potentials.

We have found that the half-neutralization voltage can be correlated with the sum of the Taft[9] substituent constants on the cyclic trimers. The following equation was obtained from a linear regression analysis of the data:

$$E_{1/2}(\text{adj.}) = 0.099\ \Sigma\sigma^* - 1.0 \qquad r = 94\%$$

The sum of the Taft substituent constants for the organic substituent on the siloxane cyclic trimers are also listed in Table 1. The Taft σ^* values employed for the groups are taken from Newman[9] with the exception of the substituent constants for the phenyl and vinyl substituents. These were values obtained from hydrogen bonding studies of triorganosilanols[10]. The reduced Taft σ^* values for these groups has been explained in terms of d_π-p_π bonding between these substituents and silicon[10,11].

It is quite clear that increased electron withdrawal by organo-substituents enhances the ease with which the siloxane structures are rearranged by basic reagents. The trend is distinct; however, the moderate correlation coefficient of 94% prohibits any meaningful discussion about attack on specific silicon atoms in the mixed siloxanes.

Qualitatively similar trends are observed for the 1,2,5-oxadisilolanes as well as the cyclic trimers. 2,2,5,5-Tetramethyl-1,2,5-oxadisilolane did not react quantitatively with the base under the conditions of the titration. In the presence of even small amounts of base this material apparently polymerized rapidly by ring opening, presumably because of its high strain energy[12]. Polymerization may have occurred

for the other strained cyclic siloxanes but if so the resulting polymer must still have maintained sufficient acid strength to utilize one mole of titrant per three moles of siloxane units. The tetramethyloxadisilolane polymer, since it possessed three electron-donating carbon groups per silicon, was too weak an acid to be titrated in this system. The absence of a definable end-point for tetrakis(trimethylsiloxy)silane and polydimethylsiloxamer may result from a slow fragmentation of the molecules in the presence of the base. Since $(Me_2SiO)_x$ is a very weak acid, determination of the end-point under optimum conditions of rapid titration would be difficult. The slow drift of the potential would tend to mask a non-distinct end-point for a slow reaction.

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