Journal of Organometallic Chemistry, 341 (1988) 199–211
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

New mechanisms for the base-catalyzed cleavage of Si–Si bonds in organopolysilanes: the base-catalyzed solvolysis of pentaphenyldisilanecarboxylic acid and pentaphenyldisilanol in ethanol/water media *,**

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(Received July 20th, 1987)

Abstract

A kinetic investigation of the base-catalyzed decomposition of pentaphenyldisilanecarboxylic acid (**1**) and pentaphenyldisilanol (**2**) in ethanol/water media is reported. The solvolysis of the Si–Si bond in **2**, which also is formed on the base-catalyzed decarbonylation of **1**, proceeds by concurrent first-order and second-order processes. At low base concentrations where the first-order process predominates, the intermediate, triphenylsilane (**3**), has been isolated. Solvent isotope effects and activation parameters have been determined. Mechanisms are proposed for the two kinetically distinguishable processes for Si–Si bond cleavage in which the pentaphenyldisilanolate ion undergoes either an internal nucleophilic displacement reaction or nucleophilic attack at Si by base in the rate-determining step.

A general mechanistic approach for the cleavage of Si–Si bonds in polysilanes by aqueous-alcoholic base is proposed in which polysilanolate ions are formed by nucleophilic attack by base at Si which undergo internal nucleophilic attack resulting in cleavage of the Si–Si bond adjacent to the anionic termini. Subsequently, polysilanolate ions are regenerated in which the number of Si atoms is reduced by one.

Introduction

The cleavage of the Si–Si bond in organopolysilanes by aqueous-alcoholic alkali is a well-known reaction in organosilicon chemistry [1–4] (eq. 1). For many

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* Dedicated to Professor Colin Eaborn in recognition of his important contributions to organometallic chemistry.

** Presented at the XVIIth Organosilicon Symposium, Schenectady, NY, April 6–7, 1984.

compounds, this reaction is quantitative and has been employed as an analytical

$$\rangle Si{-}Si\langle + 2\,ROH \xrightarrow{RO^-} 2\,\rangle SiOR + H_2 \qquad (1)$$

(R = H and/or alkyl)

method for the determination of the number of Si–Si bonds present.

A kinetic study of the base-catalyzed alcoholysis of the Si–Si bond in alkoxymethyldisilanes in alcoholic media containing sodium alkoxide has been reported by Taketa et al. [5]. This reaction was found to be first order with respect to both the disilane and alkoxide ion. The rate-determining step is proposed to involve nucleophilic attack at silicon by alkoxide ion.

This paper covers the overall process for the decomposition of pentaphenyldisilanecarboxylic acid (**1**) to triphenylsilanol, diphenylsilanediol, and their equilibration products, and the intermediates formed. However, the emphasis of this paper is on a kinetic study of the base-catalyzed solvolysis of the Si–Si bond in pentaphenyldisilanol (**2**), an intermediate formed on the decarbonylation of **1**. The mechanistic implications of this study for the base-catalyzed solvolysis of polysilanes in solvent systems which lead to intermediates containing the structural unit, $\rangle Si{-}Si{-}OH$, are discussed. A mechanistic study of the base-catalyzed decarbonylation of organosilanecarboxylic acids, an intramolecular process, will be reported in a subsequent paper [6].

Experimental

General

Analyses were performed by Analytische Laboratorien, Elbach, West Germany. The following materials were used in the synthetic and kinetic studies: triphenylchlorosilane (Aldrich); diphenyldichlorosilane, b.p. 164–165 °C/11 mmHg, (Petrarch); lithium wire (Lithium Corp. of America); deuterium oxide, 99.7% D, (Aldrich); ethanol-*d*, 99.5% D, (Aldrich); ethanol, 95%, b.p. 78 °C, (U.S. Industrial Chemicals Co.).

NMR spectra were recorded at 60 MHz on a Hitachi Perkin–Elmer R-600 spectrometer with TMS as an internal standard. IR spectra were recorded on a Beckman IR-20 spectrophotometer, polystyrene standard, and UV spectra on a Cary 14 spectrophotometer.

Preparation of pentaphenyldisilanecarboxylic acid (1)

A modification of the procedure reported by Steward et al. [7] was used to prepare **1**. Pentaphenyldisilanyllithium was prepared in one step by adding a THF solution (70 ml) of triphenylchlorosilane, 20.0 g, 0.068 mol, and diphenyldichlorosilane, 17.2 g, 0.068 mol, dropwise to lithium metal pieces, 3.5 g, 0.50 g-atom, and THF, 50 ml. After stirring overnight, the reaction mixture was carbonated and the crude acid, **1**, 26.0 g, 0.053 mol, m.p. 139–157 °C dec., a 78% yield, was isolated as described previously. Several successive recrystallizations from benzene/petroleum ether gave a sample of **1** of high purity, m.p. 188–190 °C dec. (lit. [7], 185–188 °C dec.); UV: λ_{max} (EtOH) (23000), 267 (6860), 274 nm (ϵ 4950).

Preparation of pentaphenyldisilanol (2)

A modification of the procedure reported by Steward et al. [7] was used to

Table 1

Kinetic data for the base-catalyzed solvolysis of the Si–Si bond in pentaphenyldisilanol (**2**) in 76.0 wt-% ethanol/water [a]

No.	Concentration (M) [b]		pH	T(°C)	$k_{obs} \times 10^3$ [c] (s^{-1})	$(\sigma) \times 10^3$ [d]
	NaOH	NaI				
1	0.002	1.107	12.21	25.00	0.330	0.005
2 [e]	0.005	1.104	12.52	25.00	0.768	0.009
3 [e]	0.011	1.098	12.99	25.00	1.33	0.03
4 [e]	0.059	1.049	13.80	25.00	2.42	0.02
5	0.132	0.974	–	25.00	2.71	0.01
6 [e]	0.276	0.833	–	25.00	2.93	0.03
7	0.550	0.559	–	25.00	3.29	0.05
8	0.850	0.249	–	25.00	3.64	0.03
9 [f]	1.109	–	–	25.00	3.96	0.05
10	0.276	0.833	–	15.00	0.921	0.004
11	0.276	0.833	–	35.00	8.48	0.02
12	1.107	0.002	–	15.00	1.29	0.02
!3	1.107	0.002	–	35.00	11.2	0.1

[a] Initial concentration of **2**, ca. 1.0×10^{-4} M. [b] Ionic strength maintained at 1.109. [c] All correlation coefficients > 0.999. [d] Standard deviation. [e] Solutions used for the spectrophotometric determinations of pK_a of **2**. A 1.109 M solution of NaI, pH 9.90, also was used. [f] Initial concentration of **2**, 3.98×10^{-5} M, 1.105 M NaOH, 0.004 M NaI, 25.00 °C, k_{obs} 3.98×10^{-3} s^{-1}.

prepare **2**. A toluene solution, 150 ml, of **1**, 9.5 g, 0.020 mol, was heated to reflux and maintained at that temperature for 44 h. On heating, carbon monoxide evolution was detected [8]. Removal of the solvent under reduced pressure afforded a yellowish-white solid. The IR spectrum (KBr) of this solid showed a band at 1722 cm^{-1} which is indicative of a carbonyl species other than **1**, most likely the formate ester, cf. [7,9]. The solid was dissolved in 150 ml of wet ether. After standing at ambient temperature for 4 days, the solution was dried, and the solvent was removed under reduced pressure yielding crude **2**, 7.5 g, 0.016 mol, m.p. 124–127.5 °C, an 80% yield. Several successive recrystallizations from heptane gave a sample of high purity, m.p. 134.5–135.5 °C (lit. [10], m.p. 134–134.5 °C, [7], m.p. 133–134.5 °C); UV: λ_{max} (EtOH) 244 (23,000), 267 (6560), 274 nm (ϵ 3820).

Rate measurements

The base-catalyzed solvolysis of **2** was carried out in a series of 76.0 wt-% ethanol/water solutions [11,12] of varying NaOH concentrations (see Table 1). The solutions were prepared at 25.0 ± 0.1 °C. The basic ethanolic solutions were standardized against hydrochloric acid and/or potassium hydrogen phthalate using phenolphthalein as the indicator. The pH of the solutions was measured as described below for the pK_a determination.

The composition of other solutions used in the kinetic studies are given in Table 2.

The rate studies for the base-catalyzed solvolysis of **2** were carried out spectrophotometrically using a Bausch and Lomb Spectronic 21 spectrophotometer equipped with a thermostatted cell compartment. Kinetic measurements were made using a wavelength setting of 273 nm at 15.00, 25.00, and 35.00 °C with a precision of ± 0.02 °C (NBS calibrated thermometer).

Table 2

Kinetic data for the base-catalyzed solvolysis of the Si–Si bond in pentaphenyldisilanecarboxylic acid (**1**) and pentaphenyldisilanol (**2**) in ethanol/water media [a]

Disilane	Concentrations (M)	pH	T(°C)	$k_{obs} \times 10^{3}$ [b] (s^{-1})	$(\sigma) \times 10^{3}$ [c]
1 [d,e]	$NaHCO_3$, 3.14×10^{-4} Na_2CO_3, 5.66×10^{-5} $NaNO_3$, 1.61×10^{-2}	12.05	45.00	1.07	0.06
2 [d]	$NaHCO_3$, 3.14×10^{-4} Na_2CO_3, 5.66×10^{-5} $NaNO_3$, 1.61×10^{-2}	12.05	45.00	1.09	0.01
2 [f]	NaOH, 0.260 NaI, 0.252	–	25.00	4.58	0.01
2 [f]	NaOH, 0.511	–	25.00	5.13	0.05
2 [g]	NaOH, 0.259 NaI, 0.253	–	25.00	5.37	0.01
2 [g]	NaOH, 0.512	–	25.00	5.99	0.02
2 [h]	KOH, 0.050	–	25.00	4.81	–

[a] Initial concentration of **1** and **2**, ca. 1.0×10^{-4} M. [b] All correlation coefficients > 0.999. [c] Standard deviation. [d] 76.0 wt-% ethanol/water, $\mu = 0.02$. [e] Base-catalyzed decarbonylation of **1** (above conditions). k_{obs} 3.61×10^{-3} s^{-1}, calculated using the Arrhenius equation (ref. 6). [f] 47.9 mol-% ethanol-d, 52.1 mol-% deuterium oxide, $\mu = 0.511$–0.512. [g] 47.9 mol-% ethanol, 52.1 mol-% water, $\mu = 0.512$. [h] 92.3 wt-% ethanol/water, $\mu = 0.050$.

Stock solutions of **2** in absolute ethanol were prepared, 5.0 mg/ml. A 30 μl aliquot was injected into a 1 cm quartz cell containing 3.3 ml of the basic ethanolic solution (ca. 1.0×10^{-4} M in **2**) in the thermostatted compartment. The absorbance of the solution was recorded as a function of time; a final absorbance, A_∞, was recorded after 20 half-lives. A Beer's law plot for **2** in 76 wt-% ethanol/water, 1.109 M in NaI, is linear over the concentration range employed in this study. First-order plots of the rate data, $\log(A - A_\infty)$ vs. T, are linear ($r > 0.999$). The first-order rate constant, k_{obs}, was calculated from the slope obtained by the method of least squares: the k_{obs} values reported are the average of at least three independent determinations (Tables 1 and 2).

Determination of pK$_a$ of 2

The method of Kemp et al. [13] was employed to determine the pK_a of **2**. The molar absorbance of the conjugate base of **2** is about 2.5 times greater than **2** at 273 nm. A series of 76.0 wt-% ethanol/water solutions of varying NaOH concentration and constant ionic strength, 1.109, (see Table 1) were used for the spectrophotometric determination of the pK_a. The pH of the solutions was determined using a Fisher Accumet (Model 291) pH meter equipped with a Beckman E-2 glass electrode. A sodium ion correction ranging from 0.05 to 0.34 was added to the pH reading, and a liquid junction potential correction factor of 0.18 was subtracted [14].

A stock solution of **2** was prepared, 1.1×10^{-2} M, in absolute ethanol. In each case, a 10 μl aliquot of the stock solution was added from a Hamilton microsyringe to 3.0 ml of the basic ethanolic solution. After mixing, the absorbance was recorded. In the more basic solutions, > 0.011 M NaOH, absorbance readings were extrapolated to zero time.

Product studies on the base-catalyzed solvolysis of 1 and 2

*(a) **1** in NH_3/NH_4Cl buffer in 95% ethanol.* To 45 ml of a 95% ethanol solution containing NH_3, 86 mmol, and NH_4Cl, 3.6 mmol, was added **1**, 0.30 g, 0.62 mmol, dissolved in 7 ml of ethanol. After 3.5 h at 35 ° C, the solution was acidified and extracted with ether. Crude **2**, 0.22 g, 0.48 mmol, a 77% yield was isolated from the ethereal solution. Recrystallization from carbon tetrachloride/petroleum ether gave a sample of high purity, m.p. 132.5–133.5 ° C (lit. [15], 134–134.5 ° C, [7], m.p. 133–134.5 ° C).

*(b) **1** in 1 M KOH in 95% ethanol.* The acid, **1**, 1.42 g, 2.92 mmol, was dissolved in 235 ml of 1 *M* KOH in 95% ethanol and allowed to stand at room temperature for 48 h. The solution was acidified and poured into distilled water. The dried ethereal extract yielded a yellowish oily solid which on recrystallization from benzene/petroleum ether gave impure diphenylsilanediol, 0.19 g, 0.88 mmol, m.p. 150–160 ° C, a 30% yield, and triphenylsilanol, 0.43 g, 1.6 mmol, m.p. 145–148 ° C, a 55% yield. Several successive recrystallizations of diphenylsilanediol from benzene/petroleum ether yielded a sample of high purity, m.p. 161–165 ° C (lit. [16], m.p. 162–166 ° C) and triphenylsilanol from carbon tetrachloride/petroleum ether, m.p. 148–150 ° C (lit. [17], m.p. 149–150 ° C).

A second sample of **1**, 1.49 g, 3.06 mmol, was added to 42 ml of 1 *M* KOH in 95% ethanol, in a round-bottom flask equipped with a stopcock, which had been cooled to -78 ° C. After evacuation of the system for 5 min, the mixture was slowly allowed to warm to room temperature over a period of 3 h. The gases evolved were transferred to an evacuated sample tube, and analyzed using an automated, on-line multicomponent gas chromatographic system [18] at the Pittsburgh Energy Technology Center: H_2, 78.1 ± 0.3; CO, 20.8 ± 0.3; N_2, 0.8; O_2, 0.3 vol-%. The above ethanolic solution, 8 ml, was acidified and the pH was adjusted to 10. On removal of the solvent under reduced pressure, a white solid was obtained. An IR spectrum (KBr) of this solid showed a broad absorption band from 1550–1630 cm^{-1} indicative of the carboxylate group.

A third sample of **1**, 0.1 g, 0.2 mmol, was added to 2 ml of 1 *M* KOH in 95% ethanol under the conditions described above. To 1 ml of this solution, 2 *M* hydrochloric acid (2 ml) was added, and the solution was separated from the precipitate after centrifugation. Using the chromotropic acid color test [10,19] the presence of formic acid was detected in this solution.

*(c) **2** in 1.1 M KOH in 95% ethanol.* To 25 ml of 1.1 *M* KOH in 95% ethanol, **2**, 0.70 g, 1.5 mmol, was added. After 24 h at room temperature, the solution was acidified and poured into distilled water. The dried ethereal extract afforded an oily solid (Found: C, 71.08; H, 5.66; Si, 11.30%).

Investigation of the intermediate in the base-catalyzed solvolysis of 2, triphenylsilane (3)

*(a) **2** in 0.050 M KOH in 92.3 wt-% ethanol.* To a solution of **2**, 2.00 g, 4.11 mmol, in 285 ml of 92.3 wt-% ethanol was added 19 ml of 0.80 *M* KOH in 92.3 wt-% ethanol. After approximately one half-life, 130 s, the reaction was quenched with 0.05 *M* hydrochloric acid, 350 ml. The above procedure was carried out in a constant temperature bath at 25.0 ° C. The resulting suspension was poured into distilled water and extracted with ether. The dried ethereal extract yielded an oily solid. Column chromatography (silica gel grade 923, 100–200 mesh, benzene/hexane solutions) was employed to isolate **3**, 0.15 g, 0.58 mmol; IR (CCl_4), 2127 cm^{-1}

(Si–H); ^{1}H NMR (CCl_4) δ 5.43 (s, 1 H), δ ca. 7.41 (m, 15 H); (Found: C, 83.11; H, 6.09. $C_{18}H_{16}Si$ calcd.: C, 83.02; H, 6.19%) and triphenylethoxysilane, 0.02 g, 0.07 mmol, m.p. 51–56 °C. The IR and NMR spectra were identical to an authentic sample of **3**. Recrystallization of the triphenylethoxysilane from absolute ethanol gave a sample of high purity, m.p. 64–66 °C (lit. [20], m.p. 65 °C).

*(b) Determination of the rate constant for the base-catalyzed solvolysis of the intermediate **3** in 0.050 M KOH in 92.3 wt-% ethanol.* Two methods were used to determine the first-order rate constant for the base-catalyzed solvolysis of the Si–H bond in **3** in 0.050 M KOH in 92.3 wt-% ethanol. Both methods are based on the observation that the first-order processes are occurring in series (see ref. 21).

The rate constant, k_{obs}, for the base-catalyzed solvolysis of the Si–Si bond in **2** in 0.050 M KOH in 92.3 wt-% ethanol was determined spectrophotometrically at 25.00 °C as described above. At this base concentration where the second-order process is not significant, the rate constant for the disappearance of **3** was calculated from the data in part (a) and k_{obs} (ref. 21, eq. 8.12).

The base-catalyzed solvolysis of **2** was conducted as described in part (**a**), 0.200–0.400 g samples (initial concentration, $A_0 = 1.3 \times 10^{-2}$ M), in 0.050 M KOH in 92.3 wt-% ethanol for varying lengths of time before quenching with hydrochloric acid: 85, 120, and 235 s. After extracting the solid material with ether, the ether was removed under reduced pressure, and an IR spectrum (CCl_4) was recorded. For each time, the areas of the absorption bands at 1431 cm^{-1} (Si–Ph) and 2127 cm^{-1} (Si–H) were determined, and the ratio of the areas of the bands, Si–H to Si–Ph, was calculated. Using the equations for two first-order processes occurring in series the rate constants were calculated from the best fit of the data.

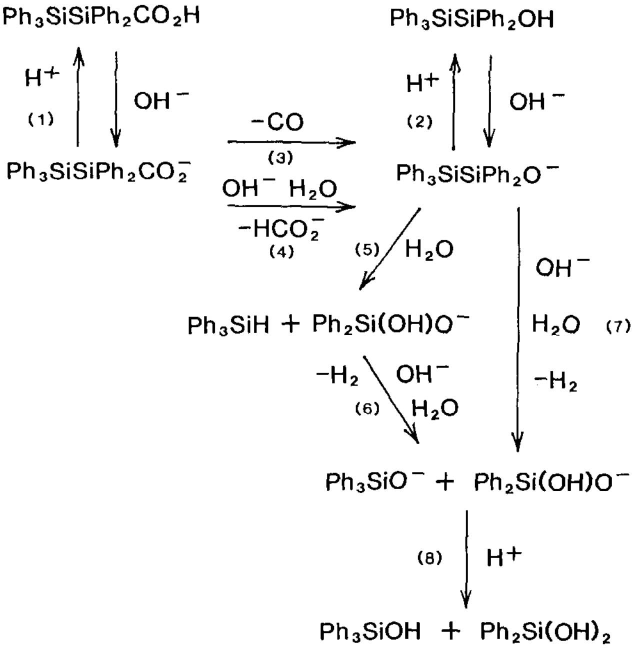
Results and discussion

Organopolysilanes which contain the structural unit, $>\mathrm{Si}-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{OH}$, or can readily form this unit on reaction, undergo facile cleavage of the Si–Si bond by basic reagents. For example, rapid cleavage of the polysilane chain occurs when silanes, Si_nH_{2n+2}, and chlorosilanes, Si_nCl_{2n+2}, are hydrolyzed under basic conditions [1]. Gilman et al. observed that Si–Si bond fission results when $Ph_3SiSiPh_2Cl$ is hydrolyzed using 1 or 5% ethanolic KOH [10]. With organohydrosilanes, the base-catalyzed solvolysis of the Si–Si and Si–H bonds often occurs concurrently [22–24].

Synthetic difficulties, because the sensitivity of the Si–Si bond toward basic conditions, were encountered by Gilman et al. when working with hydroxy-functional polysilanes [25]. When 1,4-dihydroxyoctaphenyltetrasilane and other closely related hydroxypolysilanes were passed through a chromatographic column containing basic alumina, products were isolated which could be accounted for if the Si–Si bond adjacent to the hydroxyl group had been cleaved.

In contrast, Kumada et al. have emphasized the large difference in reactivity of the Si–H and Si–Si bonds toward alcoholic alkali when these bonds are present in separate species [26]. They estimated that solvolysis of the Si–H bond in $Me_2(EtO)SiH$ is about 10^4 times faster than of the Si–Si bond in $Me_2(EtO)SiSi(OEt)Me_2$.

In this paper, a study of the decomposition of pentaphenyldisilanecarboxylic acid (**1**) and pentaphenyldisilanol (**2**) in basic ethanol/water solutions is reported with



Scheme 1. Diagram for the base-catalyzed decomposition of pentaphenyldisilanecarboxylic acid (**1**).

particular emphasis on a kinetic study of the base-catalyzed cleavage of the Si–Si bond in **2**. A diagram of the base-catalyzed decomposition of **1** in ethanol/water media is shown in Scheme 1. The studies on which this diagram is based are given below.

Intermediates and products

In the presence of basic ethanol/water, **1** decarbonylates to yield **2** via the conjugate-base forms (Scheme 1, reaction 3). In order to isolate **2**, the reaction must be carried out under mild conditions where appreciable Si–Si bond cleavage does not occur. The disilanol, **2**, was isolated in a 77% yield when the decarbonylation reaction was conducted in an NH_3/NH_4Cl buffered ethanol/water solution. The base-catalyzed decarbonylation of organosilanecarboxylic acids has been studied by Brook and Gilman [17]. A mechanistic study of this intramolecular decarbonylation will be reported in a subsequent paper [6,27].

Two solid products, triphenylsilanol (55%) and diphenylsilanediol (30%), were isolated when the solvolysis of **1** was performed in 1 *M* KOH in 95% ethanol. Equilibration products of the above silanols, i.e., siloxanes and ethoxysilanes, are probably formed under the reaction conditions but were not isolated.

The gaseous products from the solvolysis of **1** in 1 *M* KOH in 95% ethanol were analyzed by gas chromatography [18]: 78.1 ± 0.3 vol-% H_2, 20.8 ± 0.3 vol-% CO. The remaining gases, O_2 and N_2, are assigned to an air impurity based on their volume ratio. Brook and Gilman reported quantitative evolution of CO when Ph_3SiCO_2H was treated with an ethanol/water solution containing NaOH [17]. Based on the above data, a process other than decarbonylation and Si–Si bond cleavage in the conjugate-base form of **1** must be occurring since a 1/1 mixture of H_2 and CO was not obtained. In a separate experiment, formic acid was detected in the reaction mixture after acidification. In a highly basic 95% ethanol solution, it is proposed that direct nucleophilic displacement of the carboxylate group from Si by OEt^- and/or OH^- becomes an important competing process (Scheme 1, 4). Similarly, Brook and Gilman found that CO was not liberated quantitatively when esters of organosilanecarboxylic acids were treated with alcoholic base and proposed a mechanism involving nucleophilic displacement of the ester group from Si by base [17].

A C/Si ratio of 6.29 was determined for the solid products isolated when **2** was dissolved in 1.1 *M* KOH in 95% ethanol and allowed to stand for 24 h. This ratio is consistent with products which contain approximately equal numbers of the Ph_3Si and Ph_2Si groups.

One of the intermediates formed on the solvolysis of **2**, triphenylsilane (**3**), has been isolated. The solvolysis of **2** was investigated in 0.050 *M* KOH in 92.3 wt-% ethanol; only the first-order process is important at this base concentration (vide infra). The reaction was allowed to proceed for approximately one half-life, 130 s at 25.0 °C, and was quenched with dilute hydrochloric acid. From the reaction mixture, **3** was isolated in a 76% yield, calculated on the basis of the model for two consecutive first-order processes using the measured rate constants, along with a small amount of triphenylethoxysilane.

Kinetic studies

All reaction rates were measured spectrophotometrically by observing the decrease in absorbance with time at 273 nm. This change in absorptivity results primarily from cleavage of the Si–Si bond which absorbs strongly in the UV region [28]. In all cases, first-order kinetics were observed at constant base concentration. The kinetic data for the base-catalyzed solvolysis of **2** in 76.0 wt-% ethanol/water at constant ionic strength are given in Table 1. The rate constants are independent of the initial concentration of **2** (Table 1, No. 9). Rate data determined using different solvent compositions including deuterated solvents are listed in Table 2.

The variation of the first-order rate constant for the solvolysis of **2**, k_{obs}, with base concentration at 25.0 °C was analyzed using the graph shown in Fig. 1. A linear relationship is observed between k_{obs} and the base concentration when $[OH^-] > 0.13$. Using the method of least squares, the slope, k_2, is 1.26×10^{-2} l mol^{-1} s^{-1} and the intercept, k_1, is 2.57×10^{-3} s^{-1} (r > 0.999).

At low base concentrations, $[OH^-] < 0.060$, k_{obs} depends on the pH of the solution as given by eq. 2. This relationship is derived from the first-order rate

$$k_{obs} = \frac{k_1}{[H^+]/K_a + 1} \tag{2}$$

expression assuming that only the conjugate-base form of **2** undergoes solvolysis. A linear regression analysis of k_{obs} vs. $1/([H^+]/K_a + 1)$, using the data from Table 1, No. 1–4, in which K_a was optimized was employed. The slope, k_1, is 2.71×10^{-3} s^{-1}, and the optimum pK_a value is 13.0 ($r = 0.998$). This value corresponds well with the pK_a determined spectrophotometrically, 13.1, under the reaction conditions.

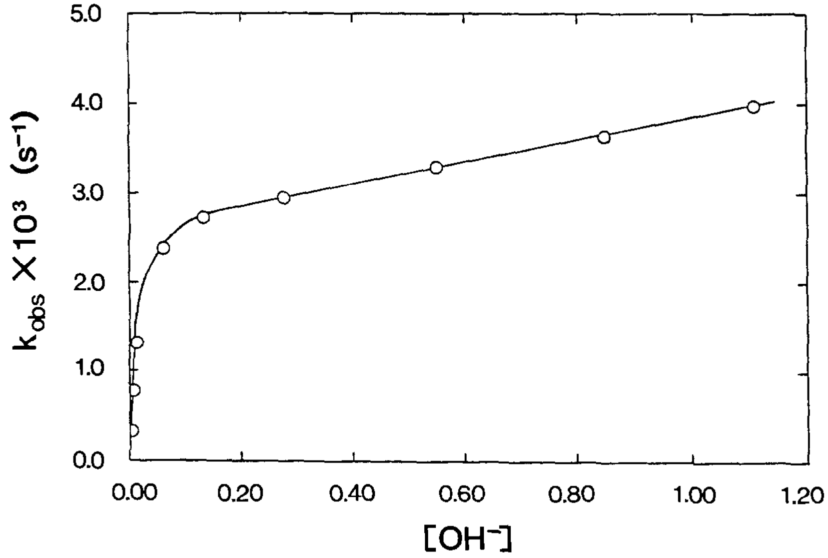


Fig. 1. Plot of the observed rate constant vs. the hydroxide ion concentration for the solvolysis of pentaphenyldisilanol (**2**) at 25.0 ° C in 76.0 wt-% ethanol/water, NaOH and NaI, $\mu = 1.11$.

Expressing eq. 2 in terms of the total base concentration, [OR$^-$], and correcting k_{obs} for the second-order term, a linear relationship is obtained between ($k_{obs} - k_2$[OR$^-$]) and $1/(K/[OR^-] + 1)$, where $K = K_s/K_a$ and K_s is the solvent dissociation constant for the reaction conditions. Applying the above described procedure and using the previously determined k_2 value and the data from Table 1, No. 4–9, the slope, k_1, is 2.88×10^{-3} s^{-1} and the optimum K value is 1.06×10^{-2} ($r = 0.999$). A pK_s value of 15.0 was calculated using the value of K and the pK_a of **2**.

The rate of decarbonylation of **1** is ca. 3.4 times faster than the cleavage of the Si–Si bond in **2** in the bicarbonate/carbonate buffer, pH 12.05, (see Table 2). Under the reaction conditions, the decarbonylation process is essentially completed after 14 min, and after this period, the rate of Si–Si bond cleavage for **1** and **2** are identical within experimental error.

The activation parameters for both the first-order and second-order solvolysis processes for **2** in 76.0 wt-% ethanol/water are given in Table 3. The data on which the calculations of the activation parameters are based were obtained at base concentration > 0.20 *M* where the curve is linear.

Table 3

Activation parameters for the base-catalyzed solvolysis of the Si–Si bond in pentaphenyldisilanol (**2**) in 76.0 wt-% ethanol/water [a]

Rate constant	$\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ [b] (e.u.)
k_1 (s^{-1})	19.8	−4.0
k_2 (l mol^{-1} s^{-1})	17.1	−14.5

[a] Calculations based on Table 1, No. 6, 9, 10–13; correlation coefficient > 0.999. [b] 25.0 ° C.

The kinetic solvent isotope effects for the base-catalyzed solvolysis of **2** were determined in a 47.9 mol-% ethanol/52.1 mol-% water solvent system prepared using either ethanol/water or ethanol-*d*/deuterium oxide. The k_{SH}/k_{SD} values for the first-order process, 1.18, and for the second-order process, 1.12, were calculated from data obtained at base concentrations > 0.20 *M* (see Table 2).

The rate of the base-catalyzed solvolysis of the intermediate, **3**, formed from **2** has been investigated in 0.05 *M* KOH in 92.3 wt-% ethanol/water at 25.0 °C. Based on the model for two first-order reactions in series [21], the upper limit for the rate constant for the solvolysis of **3** was calculated, $k_1 < 2.2 \times 10^{-2}$ s^{-1}, using the measured rate constant for the solvolysis of **2** and the amount of **3** isolated upon quenching the reaction after 130 s.

The rate constant of the solvolysis of **3**, $k_1 = 1 \times 10^{-2}$ s^{-1}, was calculated from the relative peak areas, Si–H to Si–Ph, observed in the IR spectra of the solids isolated after three different reaction periods using the model for two consecutive first-order reactions. The rate constant obtained for the solvolysis of **3** is in agreement with the value determined by interpolation of the rate data reported by Schott et al. [22] for **3** in 0.01 *M* KOH in 93.7 wt-% ethanol/water at 25 °C corrected for salt effects [29], $k_1 = 1.6 \times 10^{-2}$ s^{-1}.

The small rate difference, 2 to 4 fold, between the Si–H bond solvolysis in **3** and the Si–Si bond solvolysis in **2** in 0.05 *M* KOH in 92.3 wt-% ethanol/water indicates the rate-accelerating effect of the substituent hydroxyl group on the Si–Si bond solvolysis by the first-order process at low base concentrations.

Mechanistic implications

The base-catalyzed solvolysis of **1** at constant base concentration, < 0.060 *M*, occurs by three consecutive first-order processes; the latter process, Si–H solvolysis, is overall second order (Scheme 1, reactions 3, 5, and 6). At higher base concentrations, the first intermediate, **2**, undergoes solvolysis by a second-order process, first order in the conjugate base of **2** and first order in base (Scheme 1, reaction 7). The mechanistic implications of this study for the basic cleavage of the Si–Si bond in **2** and the basic cleavage of the Si–Si bonds in polysilanes are discussed below.

The proposed mechanism for the base-catalyzed solvolysis of **2** which are consistent with the kinetic data and the intermediates and products isolated are presented in Scheme 2. Mechanisms 1a and 1b are indistinguishable kinetically. For mechanism 1a, the dependency of k_{obs} on the $[H^+]$ is given by eq. 2. Similarly, an expression based on mechanism 1b can be derived and is given in eq. 3, where K_a is the ionization constant of **2** and K_s is the solvent dissociation constant for the reaction conditions.

$$k_{obs} = \frac{k_2(K_s/K_a)}{[H^+]/K_a + 1} \qquad (3)$$

The slow step in mechanism 1a is proposed to proceed via internal nucleophilic displacement of the Ph_3Si^- entity from the silanolate ion yielding the intermediates **3**, by reaction of the departing ion with the solvent, and diphenylsilanone [30]. The diphenylsilanone reacts rapidly with the solvent in a subsequent step yielding diphenylsilanediol, and **3** undergoes base-catalyzed solvolysis yielding hydrogen gas and triphenylsilanol. Recently, Eaborn et al. have proposed a similar mechanism involving internal nucleophilic displacement within a silanolate ion based on kinetic

Mechanism 1a

$Ph_3SiSiPh_2O^- + H_2O \rightarrow Ph_3SiH + [Ph_2Si{=}O] + OH^-$ (slow)

$[Ph_2Si{=}O] + H_2O \rightarrow Ph_2Si(OH)_2$

$Ph_3SiH + H_2O + OH^- \rightarrow Ph_3SiOH + H_2 + OH^-$

Mechanism 1b

$Ph_3SiSiPh_2OH + H_2O + OH^- \rightarrow Ph_3SiH + Ph_2Si(OH)_2 + OH^-$ (slow)

$Ph_3SiH + H_2O + OH^- \rightarrow Ph_3SiOH + H_2 + OH^-$

Mechanism 2

$Ph_3SiSiPh_2O^- + H_2O + OH^- \rightarrow Ph_3SiOH + [HPh_2SiO^-] + OH^-$ (slow)

$[HPh_2SiO^-] + H_2O \rightarrow [Ph_2Si{=}O] + H_2 + OH^-$

$[Ph_2Si{=}O] + H_2O \rightarrow Ph_2Si(OH)_2$

Scheme 2. Proposed mechanisms for the base-catalyzed solvolysis of pentaphenyldisilanol (**2**). (In the above mechanisms, EtOH and OEt^- may compete with H_2O and OH^-.)

and structure-reactivity studies (basic methanolic solutions) of Si–C and Si–I bond cleavage in compounds which are expected to yield silanolate ion intermediates [31,32]. Chojnowski et al. also have suggested that a similar mechanism is applicable to the anionic polymerization of cyclic siloxanes [33].

In mechanism 1b, the slow step is a bimolecular process involving nucleophilic attack by base at the Si bonded to the hydroxyl group yielding diphenylsilanediol and, as presented above, the departing Ph_3Si^- ion reacts with the solvent to form **3**.

Since the kinetic expressions for k_{obs} for mechanisms 1a and 1b show the same dependence on the acid and base concentrations, other data must be employed to distinguish between the two possibilities. The entropy of activation and kinetic solvent isotope effect provide a means of discriminating between the two proposed mechanisms for the first-order process.

The entropy of activation determined for the cleavage of the Si–Si bond in **2** by the first-order process is −4.0 e.u. This negative value is too small to be consistent with a bimolecular process involving nucleophilic substitution at Si. Reactions involving substitution at Si by OH^- and OR^- generally have entropies of activation in the range, −10 to −50 e.u. [34]. Taketa et al. have reported that the entropies of activation for nucleophilic substitution at Si in alkoxymethyldisilanes by OR^- in ROH, where R = Me or Et, vary from −13 to −22 e.u. [5]. In this study, $\Delta S^{\ddagger}$ is −14.5 e.u. for the solvolysis of **2** by a second-order process. The observed entropy of activation for the first-order process is more in line with a unimolecular mechanism in which the activated complex is more ordered than the reactant. In this regard, the entropy of activation for the decarbonylation of **1**, which proceeds via an intramolecular elimination of carbon monoxide from the conjugate-base form, is −6.4 e.u. [6].

The kinetic solvent isotope effect for the first-order process, $k_{SH}/k_{SD} = 1.18$, is more easily explained in terms of mechanism 1a than 1b. A unimolecular process in which there is an interaction of the departing Ph_3Si^- ion with the solvent in the rate-determining step could account for the observed effect [35]. Reactions involving nucleophilic attack at Si by OR^-, where R = H or Me, generally have k_{SH}/k_{SD} values ca. 0.5 if solvent does not react with the departing anion in the rate-controlling step [36–39]. Solvent isotope effects close to this value are reported for reactions involving substitution at Si where Ph_3C^- and Ph_3Ge^- are the departing anions [36,37].

The second-order process, Scheme 2, mechanism 2, is proposed to proceed via a slow bimolecular step involving nucleophilic substitution by base at Si in the silanolate ion, the conjugate form of **2**. Most probably, the base will attack the Si farthest from the negative charge yielding triphenylsilanol, diphenylsilanolate ion, and the conjugate base of the solvent. In a subsequent step, the diphenylsilanolate ion undergoes an internal nucleophilic displacement, as described above, in which the solvent is involved to accept the departing hydride ion yielding diphenylsilanone, hydrogen gas, and the conjugate base of the solvent. The diphenylsilanone formed in the second step reacts rapidly with the solvent yielding diphenylsilanediol.

The entropy of activation obtained for the second-order process, −14.5 e.u., is consistent with a bimolecular mechanism which involves nucleophilic substitution at Si by OR^- and falls in the range reported by Taketa et al. for the solvolysis of alkoxymethyldisilanes in basic alcoholic media [5].

The kinetic solvent isotope effect for the second-order process, $k_{SH}/k_{SD} = 1.12$, is much larger than would be expected for a reaction involving nucleophilic substitution at Si by OR^- if the departing anion does not react with solvent in the rate-controlling step. The observed solvent isotope effect suggests that electrophilic assistance is required for departure of the dinegative anion and that proton transfer from the solvent occurs in a concerted manner in the rate-determining step [40,41].

Based on the data obtained in this study and other reported studies, a general mechanistic approach for the cleavage of Si–Si bonds in polysilanes by aqueous-alcoholic base is presented below. The initial step is proposed to involve a bimolecular nucleophilic substitution process in which base attack occurs at a Si atom in the polysilane yielding polysilanolate ions and hydrogen gas as the products (eq. 4). At low base concentrations, the polysilanolate ions formed will undergo internal nucleophilic attack resulting in the cleavage of the Si–Si bonds adjacent to the anionic termini and regeneration of the polysilanolate ions in which the number of Si atoms has been reduced by one. This process will continue, resulting in the "unzipping" of the polysilanolate ions from the anionic ends. At higher base concentrations, the bimolecular process for Si–Si bond cleavage becomes competitive with the unimolecular process. The attack by base at Si may occur at other positions in the polysilane generating additional polysilanolate ions.

$$\equiv Si{-}Si{-}Si{-}Si\equiv \xrightarrow[ROH/H_2O]{OH^-} 2\ \equiv Si{-}Si{-}O^- + H_2 \qquad (4)$$

Acknowledgment

We wish to thank Mr. Joseph P. Hackett of the Pittsburgh Energy Technology Center for assistance in carrying out the gas chromatographic analysis.

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