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Reactivity of Lithium Alkylamide toward Vinylsilane Derivatives

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Kinetic studies concerning the addition reactions of lithium diethylamide (Et_2NLi) to several vinylsilane derivatives, such as $H_2C{=}CH{-}Si(CH_3)_2X$ [X: methyl, phenyl, ethoxy, 2-(diethylamino)ethyl and vinyl], and $H_2C{=}CH{-}Si(CH_3)_2OSi(CH_3)_2X$ [X: 2-(diethylamino)ethyl and vinyl], were carried out. The reactivity of vinylsilane derivatives toward nucleophile was strongly influenced by the nature of the substituents on the Si atom. The reactivity of trimethylvinylsilane [rate constant k (trimethylvinylsilane; cHx; 50 °C)$=2.9\pm0.2\cdot10^{-4}$ dm^3 mol^{-1} s^{-1}] was found to be of the same order of magnitude as that of para-alkyl-substituted styrenes, such as 4-methylstyrene [k (4-methylstyrene; cHx; 50 °C)$=3.2\cdot10^{-4}$ dm^3 mol^{-1} s^{-1}]. The reactivities of vinylsilane compounds having an aryl substituent, e.g. dimethylphenylvinylsilane [k (dimethylphenylvinylsilane; cHx; 50 °C)$=14.8\pm0.3\cdot10^{-4}$ dm^3 mol^{-1} s^{-1}] and dimethyldivinylsilane [k (dimethyldivinylsilane; cHx; 50 °C)$=14.8\pm0.6\cdot10^{-4}$ dm^3 mol^{-1} s^{-1}], were higher than that of trialkyl-substituted vinylsilane. This fact may be explained by a π-conjugation between the phenyl (or vinyl) and vinyl groups through an empty d-orbital of the Si atom. A vinylsilane compound having a 2-(dialkylamino)ethyl substituent, [2-(diethylamino)ethyl]dimethylvinylsilane, showed unique reactivity toward lithium diethylamide, indicating that the β-nitrogen atom plays an important role regarding the reactivity of the vinyl group. In the reaction between lithium diethylamide and vinylsilane having an ethoxyl group, an addition reaction to the vinyl group and a cleavage reaction of the Si–O linkage proceeded concurrently. No cleavage reaction, however, proceeded in the reaction of lithium diethylamide with vinylsilane compounds having a disiloxane linkage. 1,1,3,3-Tetramethyl-1,3-divinyldisiloxane exhibited a much higher reactivity than did the other vinylsilane compounds.

In order to design new polymeric materials having the desired structures, it is very important to have a clear relation between the structure and reactivity of vinyl monomers. Since Szwarc discovered the concept of the living anionic polymerization of vinyl monomers,[1] the reactivities of conjugated monomers, such as styrene and diene in the anionic polymerizations have been widely studied.[2] One of the authors, Tsuruta, has been studying for a long time the addition reactions of lithium alkylamides with conjugated olefins, such as dienes, styrene, and divinylbenzene.[3]

Since the reactivity of nonconjugated vinyl monomers toward nucleophiles is much lower than that of conjugated ones, the anionic polymerizations of the former monomers are limited only under special conditions. For example, ethylene is not polymerized by butyllithium alone, but is polymerized by butyllithium complexed with *N,N,N′,N′*-tetramethylethylenediamine to form the corresponding oligomers.[4] In 1963 Nametkin et al. discovered that vinylsilane compounds exhibit anionic polymerizability, even when butyllithium is used solely as an initiator.[5] There have, however, been only few reports concerning quantitative analyses of the reactivity of vinylsilane compounds. Actually, only a few monomer reactivity ratios were determined in anionic copolymerizations between vinylsilane compounds and styrene or dienes.[6]

This paper reports on studies concerning the reactivity of five vinylsilane derivatives toward nucleophile using lithium diethylamide.

Experimental

All procedures were carried out under a nitrogen or argon atmosphere so as to eliminate both oxygen and moisture.

Materials. Commercial tetrahydrofuran (THF), cyclohexane (cHx), and diethylamine were purified by conventional methods.[7] Vinylsilane compounds were supplied by Shin-Etsu Chemical Co., Ltd., and purified by fractional distillation over calcium hydride [bp: trimethylvinylsilane (**1a**), 54—55 °C/760 mmHg; dimethylphenylvinylsilane (**1b**), 80—82 °C/20 mmHg; ethoxydimethylvinylsilane (**1c**), 99—100 °C/760 mmHg; dimethyldivinylsilane (**2a**), 81—82 °C/760 mmHg; 1,1,3,3-tetramethyl-1,3-divinyldisiloxane (**2b**), 73 °C/80 mmHg (1 mmHg=133.322 Pa)]. Butyllithium (supplied by Asahi Chemical Industry Co.) was used as a hexane solution, the concentration of which was determined by Gilman's double-titration method.[8]

Addition Reaction of Lithium Diethylamide to Trimethylvinylsilane (1a). One of the representative procedures for addition reactions between lithium diethylamide and **1a** is described. To a stirred cyclohexane solution (25.5 ml) of diethylamine (Et_2NH; 10.05 g; 137.5 mmol), a hexane solution of butyllithium (7.8 ml; 12.5 mmol; 1.6 mol dm^{-3}) and benzene [as internal standard (1.0 ml)] were added. After agitation for a few minutes for the formation of lithium diethylamide (Et_2NLi), 12.5 mmol (1.25 g) of **1a** was added ([**1a**]$_0$/[Et_2NH]$_0$/[Et_2NLi]$_0$=0.25/2.5/0.25 (mol dm^{-3})). The mixture was allowed to react for several hours at 50 °C. Every few min-

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utes, a small aliquot of the mixture was sampled out, and analyzed directly by gas chromatography [Column: PEG-20M (5%; 60/80 Mesh; 6 mmϕ·4 m; column temp: 70 °C); Carrier: He (40 ml min^{-1})] toward **1a** and [2-(diethylamino)ethyl]-trimethylsilane (**3a**). Preparative purification of **3a** was carried out by fractional distillation under reduced pressure (bp: 71 °C/21 mmHg). The yield of **3a** was 80% at 7 h. **3a**: ^{1}H NMR δ=−0.05 (9H, s), 0.65 (2H, t), 1.00 (6H, t), and 2.50 (6H, m); GC t_R=7.8 min.

Addition Reaction of Lithium Diethylamide to Dimethylphenylvinylsilane (1b). One of the representative procedures for addition reactions between lithium diethylamide and **1b** is described. A cyclohexane (25.0 ml) solution of Et_2NLi (12.5 mmol) and Et_2NH (125 mmol) was prepared in a way similar to that stated above. Toluene (1 ml) was used as an internal standard for GC analysis. After the addition of 12.5 mmol (2.03 g) of **1b**, the mixture was allowed to react for several hours at 50 °C ([**1b**]$_0$/[Et_2NH]$_0$/[Et_2NLi]$_0$=0.25/2.5/0.25 (mol dm^{-3})). Every few minutes a small aliquot of the mixture was sampled out and directly analyzed by gas chromatography [Column: OV-1 (2%; 60/80 Mesh; 6 mmϕ·2 m; column temp: 80—250 °C (10 °C min^{-1})); Carrier: He (40 ml min^{-1})] toward **1b** and [2-(diethylamino)ethyl]dimethylphenylsilane (**3b**). The yield of **3b** was 95% at 3 h. **3b**: GC t_R=10.5 min; GC-MS(EI) m/z 235.

Addition Reaction of Lithium Diethylamide to Ethoxydimethylvinylsilane (1c). A cyclohexane (26.2 ml) solution of Et_2NLi (12.5 mmol) and Et_2NH (125 mmol) was prepared in a way similar to that stated above. After the addition of 12.5 mmol (1.63 g) of **1c**, the mixture was allowed to react for 1 hour at 50 °C ([**1c**]$_0$/[Et_2NH]$_0$/[Et_2NLi]$_0$=0.25/2.5/0.25 (mol dm^{-3})). The mixture was analyzed directly by gas chromatography [Column: OV-1 (2%; 60/80 Mesh; 6 mmϕ·2 m; column temp: 80—165 °C (10 °C min^{-1})); Carrier: He (40 ml min^{-1})] toward **1c**, 1 : 1 adduct, [2-(dimethylamino)ethyl]-ethoxydimethylsilane (**3c**) [GC t_R=6.2 min; GC-MS(EI) m/z 203], and diethylaminodimethylvinylsilane [GC t_R=3.2 min; GC-MS (EI) m/z 157].

Addition Reaction of Lithium Diethylamide to Dimethyldivinylsilane (2a). One of the representative procedures for the addition reactions between lithium diethylamide and **2a** is described. A cyclohexane (25.4 ml) solution of Et_2NLi (12.5 mmol) and Et_2NH (125 mmol) was prepared in a way similar to that stated above. *o*-Xylene (1 ml) was used as an internal standard for GC analysis. After the addition of 12.5 mmol (1.40 g) of **2a**, the mixture was allowed to react for several hours at 50 °C ([**2a**]$_0$/[Et_2NH]$_0$/[Et_2NLi]$_0$=0.25/2.5/0.25 (mol dm^{-3})). Every few minutes a small aliquot of the mixture was sampled out and analyzed directly by gas chromatography [Column: OV-1 (2%; 60/80 Mesh; 6 mmϕ·1 m; column temp: 80—165 °C (10 °C min^{-1}); Carrier: He (40 ml min^{-1})] toward **2a**, [2-(diethylamino)ethyl]dimethylvinylsilane (**4a**), and bis[2-(diethylamino)ethyl]dimethylsilane (**5a**). Purification of **4a** and **5a** was carried out by fractional distillation under reduced pressure (**4a**: bp: 57 °C/0.1 mmHg; **5a**: bp: 83—84 °C/0.1 mmHg). The change in the yields of products **4a** and **5a** as a function of time is shown in Fig. 1. **4a**: ^{1}H NMR δ=0.00 (6H, s), 0.65 (2H, t), 1.00 (6H, t), 2.50 (6H, m), and 5.60—6.20 (3H, m); GC t_R=3.0 min; GC-MS(EI) m/z 185. **5a**: ^{1}H NMR δ=−0.05 (6H, s), 0.65 (4H, t), and 1.00 (12H, t), 2.50 (12H, m)); GC t_R=7.6 min; GC-MS(EI) m/z 258.

Addition Reaction of Lithium Diethylamide to 1,1,3,3-Tetramethyl-1,3-divinyldisiloxane (2b). One of the representative procedures for addition reactions between lithium diethylamide and **2b** is described. A cyclohexane (24.4 ml) solution of Et_2NLi (12.5 mmol) and Et_2NH (125 mmol) was prepared in a way similar to that stated above. *o*-Xylene (1 ml) was used as an internal standard for GC analysis. After the addition of 12.5 mmol (2.33 g) of **2b**, the mixture was allowed to react for several hour at 50 °C ([**2a**]$_0$/[Et_2NH]$_0$/[Et_2NLi]$_0$=0.25/2.5/0.25 (mol dm^{-3})). Every few minutes a small aliquot of the mixture was sampled out and analyzed directly by gas chromatography [Column: OV-1 (2%; 60/80 Mesh; 6 mmϕ·2 m; column temp: 100—300 °C (10 °C min^{-1}); Carrier: He (40 ml min^{-1})] toward **2b**, 1,1,3,3-tetramethyl-1-[2-(diethylamino)ethyl]-3-vinyldisiloxane (**4b**), and 1,1,3,3-tetramethyl-1,3-bis[2-(diethylamino)ethyl]disiloxane (**5b**). Purification of **4b** and **5b** was carried out by fractional distillation under reduced pressure (**4b**: bp: 54 °C/0.06 mmHg; **5b**: bp: 83—84 °C/0.06 mmHg). The change in the yields of products **4b** and **5b** as a function of time is shown in Fig. 2. **4b**: ^{1}H NMR δ=−0.05 (6H, s), 0.00 (6H, s), 0.65 (2H, m), 1.00 (6H, t), 2.50 (6H, m), and 5.60—6.20 (3H, m); GC t_R=2.9 min; GC-MS(EI) m/z 259. **5b**: ^{1}H NMR δ=−0.05 (12H, s), 0.65 (4H, t), 1.00 (12H, t), and 2.50 (12H, m); GC t_R=13.1 min; GC-MS(EI) m/z 332.

Measurements. ^{1}H NMR spectra were observed on a Varian VXR-500S or JEOL GX-270 spectrometer at room temperature. ^{13}C NMR spectra were observed on a JEOL FX-90Q spectrometer. Gas chromatograms were taken with a Hitachi 063 or Shimadzu gas chromatograph (GC-14A). GC/Mass spectra were obtained using a JEOL-DX303.

Results and Discussion

Reaction of Lithium Diethylamide with Trimethylvinylsilane (1a) in the Presence of Diethylamine. Nametkin et al. reported that the reaction of lithium diethylamide with trimethylvinylsilane (**1a**) gave a 1 : 1 addition product [2-(diethylamino)ethyl]trimethylsilane (**3a**) in good yield.[9] Details concerning the reaction, however, were not revealed. In the course of our study concerning the reactivity of lithium alkylamide in addition reactions, we investigated in greater detail the reaction between lithium diethylamide and **1a**.

In the reaction between lithium diethylamide and **1a**, a new product, which had a molecular weight of 173 (determined from the GC/Mass spectrum), was formed. From the ^{1}H NMR spectrum, the product was found to be a 1 : 1 adduct between lithium diethylamide and **1a**. The GPC chromatogram of the reaction mixture showed that no polymerization took place. On the basis of these results, it is confirmed that a 1 : 1 addition reaction took place selectively in the reaction between lithium diethylamide and **1a** in the presence of diethylamine, Eq. 1.

$$(CH_3CH_2)_2NLi + \mathbf{1} \xrightarrow{(CH_3CH_2)_2NH} \underset{\mathbf{3}}{(CH_3CH_2)_2NCH_2CH_2Si(CH_3)_2X} \quad (1)$$

	X
3a	CH_3
3b	C_6H_5
3c	OCH_2CH_3

Table 1. Second-Order Rate Constants for the Addition Reaction of Lithium Diethylamide with Trimethylvinylsilane (**1a**) in the Presence of Diethylamine[a)]

Run	Solvent	Temp / °C	$10^4 \times k$ / $dm^3\,mol^{-1}\,s^{-1}$
1	cHx	40	1.1±0.1
2	cHx	50	2.9±0.2
3	cHx	60	6.4±0.6
4	THF	30	4.4±0.3
5	THF	40	10.4±0.5
6	THF	50	21.2±0.8

a) $[\mathbf{1a}]_0/[Et_2NLi]_0/[Et_2NH]_0=0.25/0.25/2.50\ mol\,dm^{-3}$.

A kinetic study of the reaction between lithium diethylamide and **1a** was carried out under several reaction conditions. From the slopes of the first order plots for the reactions, the rate constants were determined. Since the concentration of lithium diethylamide was considered to be constant throughout the reaction,[10] the second-order rate constants were determined simply by dividing the first-order rate constants by the lithium diethylamide concentration; the results are listed in Table 1. The rate constant for the reaction of lithium diethylamide with **1a** [k (**1a**; cHx; 50 °C)$=2.9\pm0.2\cdot10^{-4}$ $dm^3\,mol^{-1}\,s^{-1}$] was of the same order as that of the para-alkyl-substituted styrenes [e.g. k (4-Methylstyrene; cHx; 50 °C)$=3.2\cdot10^{-4}$ dm^3 $dm^3\,mol^{-1}\,s^{-1}$] under the same reaction conditions. Such a reactivity of trimethylvinylsilane toward nucleophile, as high as that of conjugated monomers, may be explained by a dπ–pπ interaction between the vinyl π-system and an empty d-orbital on the Si atom.[10]

Reaction of Lithium Diethylamide with Dimethylphenylvinylsilane (1b) in the Presence of Diethylamine. In the reaction between lithium diethylamide and dimethylphenylvinylsilane (**1b**), a 1 : 1 adduct, [2-(diethylamino)ethyl]dimethylphenylsilane [**3b** in Eq. 1], was the sole product. From the slope of the first-order plots of the reaction, it was found that the rate constant ([k (**1b**; cHx; 50 °C)$=14.8\pm0.3\cdot10^{-4}$ $dm^3\,mol^{-1}\,s^{-1}$] was about 6-times higher than that of **1a** under the same reaction conditions. This fact may be explained by a p-conjugation between vinyl and phenyl groups through an empty d-orbital on the Si atom.[1a)]

Reaction of Lithium Diethylamide with Dimethyldivinylsilane (2a) in the Presence of Diethylamine. The reactivity of divinylsilane compounds (**2a** and **2b**) toward lithium diethylamide was investigated in comparison with the reactivity of monovinylsilane derivatives.

The reaction between lithium diethylamide and dimethyldivinylsilane (**2a**) gave two new products. The molecular weights of these two products were determined to be 185 and 258 by GC/Mass spectroscopy, which corresponded, respectively, to the 1 : 1 and 1 : 2 adducts of diethylamine to **2a**. From a ^1H NMR analysis of these products after purification by distillation under reduced pressure, it was confirmed that they were [2-(diethylamino)ethyl]dimethylvinylsilane [**4a** in Eq. 2] and bis[2-(diethylamino)ethyl]dimethylsilane [**5a** in Eq. 2], respectively.

$$(CH_3CH_2)_2NLi + 2 \xrightarrow{(CH_3CH_2)_2NH} (CH_3CH_2)_2N\text{-}CH_2CH_2\text{-}Si(CH_3)_2\text{-}[O\text{-}Si(CH_3)_2]_n\text{-}CH{=}CH_2$$

4

$$+\ (CH_3CH_2)_2N\text{-}CH_2CH_2\text{-}Si(CH_3)_2\text{-}[O\text{-}Si(CH_3)_2]_n\text{-}CH_2CH_2\text{-}N(CH_2CH_3)_2 \quad (2)$$

5

	n
4a, **5a**	0
4b, **5b**	1

Figure 1 shows the time-dependent changes in the concentrations of **2a** and products **4a** and **5a** in the reaction system. During the early stage, the concentration of **4a** increases with time. After the maximum concentration point of **4a**, the concentration of **5a** increases with a decrease of the **4a** concentration, which shows the present system to be a typical consecutive reaction. According to the fundamental equations for

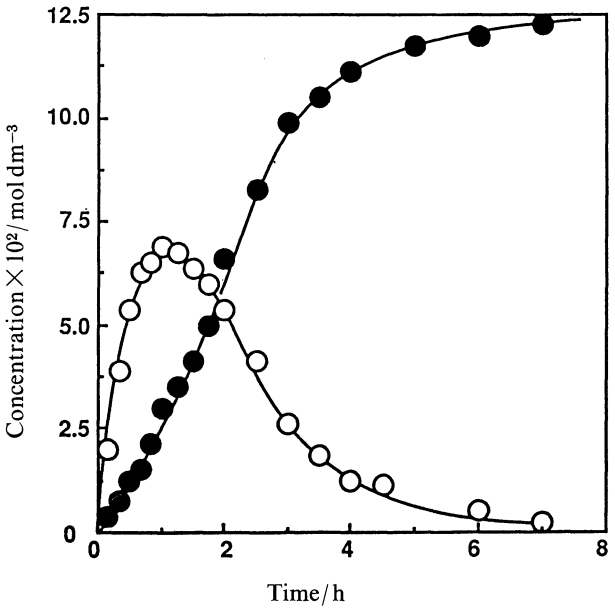


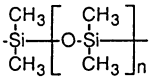
Fig. 1. Change in the concentrations of 1 : 1 (**4a**; ○) and 1 : 2 (**5a**; ●) adducts in the addition reaction between lithium diethylamide and dimethyldivinylsilane (**2a**) as a function of time. ($[\mathbf{2a}]_0/[Et_2NLi]_0/[Et_2NH]_0=0.125/0.125/1.25$ $mol\,dm^{-3}$; Solvent: Cyclohexane; Temperature: 50 °C. The lines in the Figure were drawn according to calculation results obtained by Eqs. 5 to 7[11]).

a consecutive reaction, a rate analysis in the addition reactions was carried out.

In the consecutive reaction, it is known that the first- and second- step rate constants [k_2 and k_4 in Eqs. 3 and 4, respectively] can be determined by a first-order plot for reactant **2** and by

$$(CH_3CH_2)_2NLi + \mathbf{2} \xrightarrow{k_2} (CH_3CH_2)_2NCH_2CHLi\text{-}R\text{-}CH{=}CH_2 \quad (3)$$

$$(CH_3CH_2)_2NLi + \mathbf{4} \xrightarrow{k_4} (CH_3CH_2)_2NCH_2CH_2\text{-}R\text{-}CHLiCH_2N(CH_2CH_3)_2 \quad (4)$$

-R-:  , where n=0 (**4a**) or n=1 (**4b**)

the maximum concentration of **4** formed, and its reaction time, respectively.[11] The rate constants (k_{2a}) were determined from the slopes of the straight lines of first-order plots for the reaction between lithium diethylamide and **2a** under several reaction conditions. The results are summarized in Table 2, together with the maximum concentration and reaction time of **4a** formed in the reaction system, as well as k_{4a} determined from these data. Since the time (t_{max}) at the maximum point was difficult to estimate accurately, rate constants k_{4a} were determined by a curve-fitting method using Eqs. 5 to 7.

$$[\mathbf{2}] = [\mathbf{2}]_0 \cdot e^{-k_2 t} \quad (5)$$

$$[\mathbf{4}] = \frac{k_2 \cdot [\mathbf{2}]_0}{k_2 - k_4} (e^{-k_4 t} - e^{-k_2 t}) \quad (6)$$

$$[\mathbf{5}] = [\mathbf{2}]_0 \left(1 + \frac{k_4}{k_2 - k_4} e^{-k_2 t} - \frac{k_2}{k_2 - k_4} e^{-k_4 t}\right) \quad (7)$$

The value of k_{4a} determined by this method was confirmed to agree fairly well with that obtained directly from a first-order plot for the reaction of lithium diethylamide toward **4a** under the same reaction conditions (Runs 3 and 5 in Table 2). From these kinetic analyses it was found that **2a** exhibited a higher reactivity toward the nucleophilic reagent than did **1a**, since **2a**, as well as **1b**, has a substituent with the p-electron system.

Vinylsilane, having 2-aminoethyl substituent, **4a**, showed unique reactivity. In a THF solution **4a** exhibited similar reactivity to **1a**, indicating that the 2-(diethylamino)ethyl group adjacent to the Si atom shows no effect on the reactivity toward lithium diethylamide. In a cyclohexane solution, on the other hand, the reactivity of **4a** toward lithium diethylamide was much higher than that of **1a**, though the mechanism has not yet been elucidated.

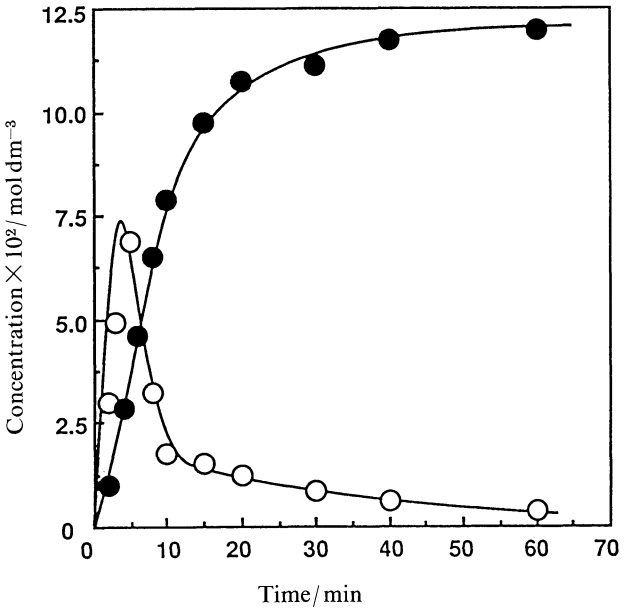


Fig. 2. Change in the concentrations of 1:1 (**4b**; ○) and 1:2 (**5b**; ●) adducts in the reaction between lithium diethylamide and 1,1,3,3-tetramethyl-1,3-divinyldisiloxane (**2b**) as a function of time. ([**2b**]$_0$/[Et_2NLi]$_0$/[Et_2NH]$_0$=0.125/0.25/2.50 (mol dm^{-3}; n=1); Solvent: Cyclohexane; Temperature: 50 °C. The lines in the Figure were drawn according to calculation results obtained by Eqs. 3 to 5[11]).

Table 2. Second-Order Rate Constants for the Addition Reaction of Lithium Diethylamide with Dimethyldivinylsilane (**2a**) in the Presence of Diethylamine[a]

Run	Solvent	Temp	t_{max}[b]	Yield$_{max}$[c]	$10^4 \times k$ (**2a**)	$10^4 \times k$ (**4a**)
		°C	*h*	%	dm^3 mol^{-1} s^{-1}	dm^3 mol^{-1} s^{-1}
1	cHx	35	3.3	55.0	5.2±0.3	2.0
2	cHx	40	2.1	55.5	8.0±0.3	3.2
3	cHx	50	0.96	51.3	16.8±0.2	7.6
4[d]	cHx	50	1.1	51.6	14.8±0.6	6.8
5[e]	cHx	50	—	—	—	8.8±0.5
6	THF	10	3.4	78.3	8.4±0.2	0.84
7	THF	30	0.81	74.0	31.2±0.2	4.4
8	THF	50	0.22	71.3	112.0±0.1	17.2

a) [**2a**]$_0$/[Et_2NLi]$_0$/[Et_2NH]$_0$=0.25/0.25/2.50 mol dm^{-3}. b) Time at the maximum concentration of [**4a**]. c) Maximum yield of [**4a**]. d) [**2a**]$_0$/[Et_2NLi]$_0$/[Et_2NH]$_0$=0.125/0.25/2.50 mol dm^{-3}. e) Data from the reaction between lithium diethylamide and **4a** isolated by distillation under reduced pressure. [**4a**]$_0$/[Et_2NLi]$_0$/[Et_2NH]$_0$=0.125/0.25/2.50 mol dm^{-3}.

Table 3. Second-Order Rate Constants for the Addition Reaction of Lithium Diethylamide with 1,1,3,3-Tetramethyl-1,3-divinyldisiloxane (**2b**) in the Presence of Diethylamine in Cyclohexane[a)]

Run	Temp	t_{max}[b)]	$Yield_{max}$[c)]	$10^4 \times k$ (**2b**)	$10^4 \times k$ (**4b**)
	°C	*h*	%	$dm^3\,mol^{-1}\,s^{-1}$	$dm^3\,mol^{-1}\,s^{-1}$
1	30	0.79	30.4	13.6±1.0	14.4
2	40	0.39	32.0	28.0±0.8	28.8
3	50	0.21	26.0	48.0±0.8	56.0

a) $[\mathbf{2b}]_0/[Et_2NLi]_0/[Et_2NH]_0=0.25/0.25/2.50$ mol dm^{-3}. b) Time at the maximum concentration of [**4b**]. c) Maximum yield of [**4b**].

Reactions of Lithium Diethylamide with Ethoxydimethylvinylsilane (1c) and 1,3,3,3-Tetramethyl-1,3-divinyldisiloxane (2b) in the Presence of Diethylamine. Kumada et al. reported that the addition and substitution reactions proceeded concurrently in the reaction between butyllithium and vinylsilanes, having alkoxyl substituent(s) on the Si atom.[12] We also confirmed the formation of both addition and substitution products in the reaction between lithium diethylamide and ethoxydimethylvinylsilane (**1c**). Although 1,1,3,3-tetramethyl-1,3-divinyldisiloxane (**2b**) has an Si–O linkage, no cleavage reaction took place in the reaction with lithium diethylamide in the cyclohexane media. Namely, only addition reactions proceeded selectively to form 1 : 1 and 1 : 2 adducts, 1,1,3,3-tetramethyl[2-(diethylamino)-ethyl]vinyldisiloxane [**4b** in Eq. 2] and 1,1,3,3-tetramethyl-1,3-bis[2-(diethylamino)ethyl]disiloxane [**5b** in Eq. 2], respectively.

As shown in Fig. 2, the time courses of the product concentrations in the reaction system between lithium diethylamide and **2b** showed a typical consecutive reaction pattern. The results obtained for the rate constants are summarized in Table 3. The reactivity of **2b** toward lithium diethylamide in cyclohexane was found to be about 3-times higher than that of **2a**, indicating the reactivity of the vinyl group in the **2b** molecule to be markedly influenced by the Si–O–Si conjugation in **2b**. The reactivity of **4b** to lithium diethylamide was of the same order as that of **2b**, indicating the absence of conjugation between the two vinyl groups in **2b**.

On the basis of these results, the reactivities of vinylsilane compounds toward lithium diethylamide are summarized as follows:

para-alkylstyrenes$\approx CH_2$=CH–Si–Alkyl$<$
CH_2=CH–Si–Aryl$<CH_2$=CH–Si–O–Si–R,
CH_2=CH–Si–Alkyl$\approx CH_2$=CH–Si–$CH_2CH_2NR_2$
(in polar media),
CH_2=CH–Si–Alkyl$<CH_2$=CH–Si–$CH_2CH_2NR_2$
(in nonpolar media).

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