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# An Addition Reaction of Diethylamine to Styrene Catalyzed by Lithium Diethylamide

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An addition reaction of diethylamine to styrene catalyzed by lithium diethylamide was found to proceed stoichiometrically to produce 1-diethylamino-2-phenylethane. The rate of the reaction was expressed by the equations: $v=k[\mathrm{Styrene}][\mathrm{Et_2NLi}]^{1.3}$ and $v=k[\mathrm{Styrene}][\mathrm{Et_2NLi}]$, the ratios of $[\mathrm{Et_2NH}]_0$ to $[\mathrm{Et_2NLi}]_0$ being 3.0 and 10 respectively. On the basis of the kinetic studies, the mechanism of the addition reaction was elucidated. The nucleophilic character of this reaction was clearly demonstrated by the $\sigma-\rho$ Hammett plot. The second-order rate constant for the addition reaction of styrene was found to be of the same order of magnitude as that of butadiene. The presence of butadiene in the reaction system showed no effect on the reactivity of styrene.

The reactions of some active hydrogen compounds with butadiene initiated by alkyllithium has recently been reported to produce interesting intermediate compounds for organic synthesis.

The reaction of diphenylmethane with butadiene initiated by the system consisting of *n*-butyllithium and a donor compound has been found to produce 5,5-diphenylpentene derivatives.[1] A stereospecific reaction takes place, on the other hand, when diethylamine is reacted with butadiene in the presence of lithium diethylamide at the $[\mathrm{Et_2NH}]_0/[\mathrm{Et_2NLi}]_0$ ratio of 3.0, the selectivity of the product, 1-diethylamino-*cis*-butene-2, being up to 99%.[2] On the basis of kinetic and spectroscopic studies, the lithium diethylamide—diethylamine (1 : 2) complex has been concluded to play an important role in this reaction.[3]

It is widely accepted that the microstructures of polydienes prepared by alkyllithium are markedly different from one another according to the nature of the solvents or complexing agents used for the polymerization reactions. The predominant formation of 1,4-structure in hydrocarbon solvents is interpreted in terms of a concerted mechanism in which the preliminary coordination of diene molecules to the organolithium species is assumed. Lewis bases used as solvents (or complexing agents) interfere with the coordination of the monomer molecules, resulting in the predominant formation of the 1,2-structure in the polymer chain.

It is also known, in the styrene-diene copolymerization initiated by alkyllithium in hydrocarbon, that the reactivity of styrene is very much enhanced in the presence of Lewis bases.

In the light of these previous results, the stereospecific addition reaction of the lithium diethylamide—diethylamine complex seems to possess some peculiar character, for the 1,4-*cis*-structure is almost exclusively formed in the addition product, even in the presence of the Lewis base. In order to make clear the nature of the lithium amide complex in more detail, the addition reactions to styrene and its derivatives were studied.

## Experimental

Most of the experiments were carried out under a purified nitrogen atmosphere in order to exclude oxygen and moisture.

*Materials.* Commercial cyclohexane, styrene, α-methylstyrene, butadiene, diethylamine, and triethylamine were purified by the usual method. *n*-Butyllithium was prepared from *n*-butyl chloride and lithium metal in purified petroleum ether and was used as a cyclohexane solution. *p*-Methylstyrene[4] and *p*-methoxystyrene[5] were synthesized according to the literature.

*Procedures.* The methods of the rate study of the addition reactions were described in an earlier publication.[3] The analyses of the addition-reaction product of diethylamine with styrene, 1-diethylamino-2-phenylethane, and of those with *p*-methylstyrene and *p*-methoxystyrene were performed by studying the infrared and proton magnetic resonance spectra.

## Results and Discussion

As has been reported previously, the addition reaction of lithium diethylamide with butadiene does not

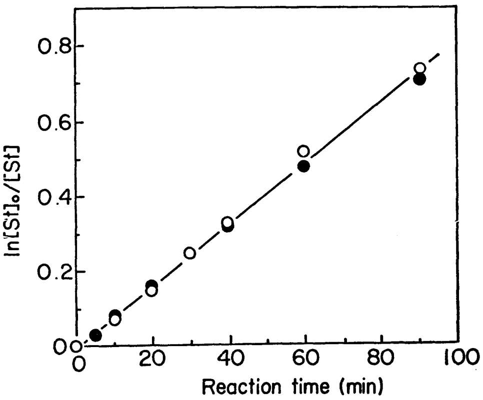

Fig. 1. First-order analyses of the reaction of $\mathrm{Et_2NH}$-$\mathrm{Et_2NLi}$ complex with styrene: dependence of styrene concentration.
$[\mathrm{Et_2NLi}]_0=0.250$ mol/l, $[\mathrm{Et_2NH}]_0/[\mathrm{Et_2NLi}]_0=3.0$ in cyclohexane at 50°C ● from [Styrene], ○ from $[\mathrm{Et_2NCH_2CH_2C_6H_5}]$.

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[1] T. Yamaguchi, T. Narita, and T. Tsuruta, *Polymer J.*, **3**, 573 (1972).

[2] N. Imai, T. Narita, and T. Tsuruta, *Tetrahedron Lett.*, **1971**, 3517.

[3] T. Narita, N. Imai, and T. Tsuruta, This Bulletin, **46**, 1242 (1973).

[4] D. T. Mowry, M. Renoll, and W. F. Huber, *J. Amer. Chem. Soc.*, **68**, 1105 (1946).

[5] C. Walling, and K. B. Wolfstirm, *ibid.*, **69**, 852 (1947).

[6] T. Asahara, M. Seno, S. Tanaka, and N. Den, This Bulletin, **42**, 2337 (1969).

proceed in the absence of dialkylamine.[2,3] A similar phenomenon was also observed in the reaction of lithium diethylamide with styrene, no addition product, 1-diethylamino-2-phenylethane, being detected until an excess of free diethylamine is present along with the lithium amide in the reaction system.

The dependence of the initial styrene concentration on the reaction rate is shown in Fig. 1. As the curves for the concentrations of the starting materials and of the addition product measured independently by means of the vapor-phase chromatography are clearly symmetrical, any possibilities of side reactions such as telomerization[6] may be ruled out. Since the first-order analyses shown in Fig. 1 stay linear until 50% conversion, the reaction rate is proportional to the first-order of the styrene concentration. The pseudo first-order rate constants are summarized in Table 1.

TABLE 1. PSEUDO FIRST-ORDER RATE CONSTANTS OF THE REACTION OF $Et_2NH$-$Et_2NLi$ COMPLEX WITH STYRENE[a]

| $[Et_2NH]_0$ mol/l | $[Et_2NLi]_0$ mol/l | $[Styrene]_0$ mol/l | $k'$ hr$^{-1}$ |
|---|---|---|---|
| 0.750 | 0.250 | 0.125 | 0.49 |
| 0.750 | 0.250 | 0.250 | 0.48 |
| 0.750 | 0.250 | 0.375 | 0.49 |

a) In cyclohexane at 50°C.

In order to determine the dependency of the reaction rate on the concentration of lithium diethylamide, the reaction rate was analyzed under a constant concentration of styrene, with the ratio of $[Et_2NH]_0$ to $[Et_2NLi]_0$ being 3.0. When the reaction rate is expressed as Eq. (1), the pseudo firstorder rate constant, $k'$, can be determined from the slopes of the straight lines in Fig. 2:

$$v = k'[\text{Styrene}] \qquad (1)$$

The slopes of the line which are obtained from the plot of log $k'$ *vs.* log$[Et_2NLi]$ should show the dependency on the lithium diethylamide concentration:

$$k' = k_8[Et_2NLi]^x \qquad (2)$$

As is shown in Fig. 3 and Table 2, the reaction rate can be expressed as Eq. (3) in the range of $[Et_2NH]_0/[Et_2NLi]_0 \geqq 10$:

$$v = k_8[\text{Styrene}][Et_2NLi] \qquad (3)$$

whereas the reaction order shows some fractional power in the cases of $[Et_2NH]_0/[Et_2NLi]_0=3.0$ ($x=1.3$) and 5.0 ($x=1.2$), as is shown in Eq. (4):

$$v = k_8[\text{Styrene}][Et_2NLi]^x \qquad (4)$$

This phenomenon may be explained in terms of the "solvent effect", because the increase in the lithium amide concentration is accompanied by an increase in the double mole quantity of diethylamine. The increase in the rate caused by the "solvent effect" may be eliminated by adjusting the total amine concentration with triethylamine. The results of the experiments in which the total amine concentration, $[Et_2NH]_0+[Et_3N]$, was kept constant are shown by a dotted line in Fig. 3. The reaction order obtained from the slope is $1.0_4$. The acceleration of the addition reaction rate observed in Fig. 3 may, therefore, be concluded to come from the "solvent effect" of amines.[7]

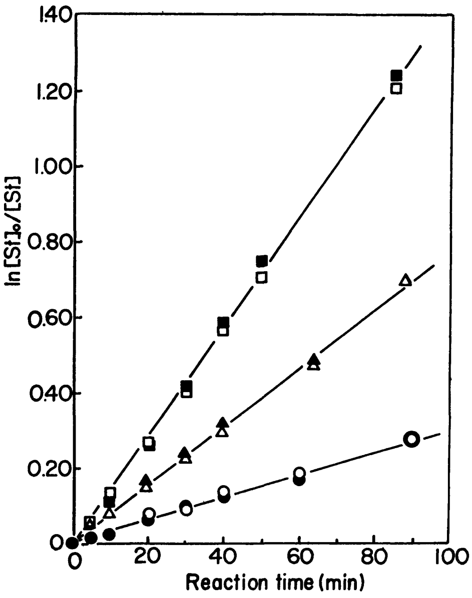

Fig. 2. Reaction of $Et_2NH$-$Et_2NLi$ complex with styrene: dependence of lithium diethylamide concentration: first-order analyses for styrene concentration.
$[St]_0=0.250$ mol/l, $[Et_2NH]_0/[Et_2NLi]_0=3.0$ in cyclohexane at 50 °C, $[Et_2NLi]_0=0.125$ mol/l (○) 0.250 mol/l (△) and 0.375 mol/l (□).
○△□ $Et_2NCH_2CH_2C_6H_5$, ●▲■ styrene.

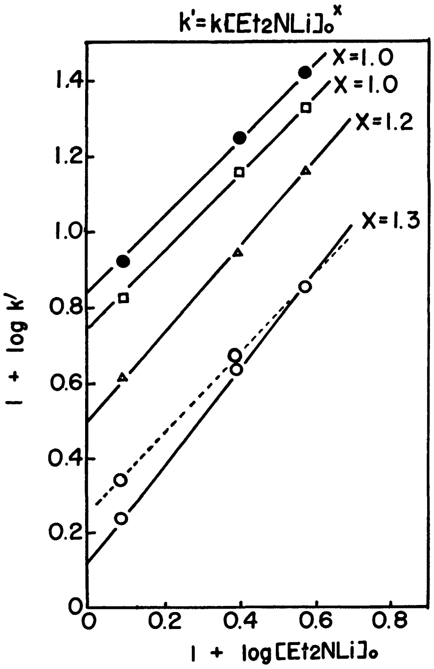

Fig. 3. Relationship between lithium diethylamide concentration and pseudo first-order rate constant.
$[Et_2NH]_0/[Et_2NLi]_0=3.0$ (○), 5.0 (△), 10 (□) and 15 (●) in cyclohexane at 50 °C
Dotted line: $[Et_2NH]_0/[Et_2NLi]_0=3.0$, $[Et_2NH]_0+[Et_3N]=0.375$ mol/l (*cf.* Fig. 2).

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[7] Possibility that the difference may come from the decrease of effective concentration of the active species by the reverse reaction of Eq. (6) might be disproved since ultraviolet spectral measurement of the reaction system showed no peak assignable to $Et_2NCH_2\overset{\ominus}{C}HC_6H_5\overset{\oplus}{Li}$.[8]

TABLE 2. REACTION KINETICS OF $Et_2NH$-$Et_2NLi$ COMPLEX WITH STYRENE[a)]

| $\frac{[Et_2NH]_0}{[Et_2NLi]_0}$ | $[Et_2NLi]_0$ mol/l | $k'$ $hr^{-1}$ | Note |
|---|---|---|---|
| 3.0 | 0.125 | 0.16 | $v=k_S[\text{Styrene}][Et_2NLi]^{1.3}$ |
| | 0.250 | 0.43 | |
| | 0.375 | 0.71 | |
| 5.0 | 0.125 | 0.41 | $v=k_S[\text{Styrene}][Et_2NLi]^{1.2}$ |
| | 0.250 | 0.88 | |
| | 0.375 | 1.46 | |
| 10 | 0.125 | 0.66 | $v=k_S[\text{Styrene}][Et_2NLi]$<br>$k_S=1.6\times10^{-3}$ l/mol·s |
| | 0.250 | 1.45 | |
| | 0.375 | 2.16 | |
| 15 | 0.125 | 0.83 | $v=k_S[\text{Styrene}][Et_2NLi]$<br>$k_S=2.0\times10^{-3}$ l/mol·s |
| | 0.250 | 1.81 | |
| | 0.375 | 2.61 | |
| 28 | 0.250 | 2.32 | $k_S=2.6\times10^{-3}$ l/mol·s |

a) $[\text{Styrene}]_0=0.250$ mol/l, in cyclohexane at 50°C.

The acceleration of the rate by the increased concentrations in the range of higher concentrations may also be seen in Table 2.

These results show that the reactivity of styrene is more sensitive to the change in the polarity of the solvent used than is that of butadiene (*cf.* Table 3).

The overall reaction scheme of the addition reaction of diethylamine with styrene can, therefore, be depicted as follows:

$$Et_2NLi + 2Et_2NH \rightarrow Et_2NLi\cdot 2Et_2NH \qquad (5)$$

$$Et_2NLi\cdot 2Et_2NH + C_6H_5CH{=}CH_2 \xrightarrow{k_S} Et_2NCH_2CHC_6H_5Li\cdot 2Et_2NH \qquad (6)$$

$$Et_2NCH_2CHC_6H_5Li\cdot 2Et_2NH + Et_2NH \longrightarrow Et_2NCH_2CH_2C_6H_5 + Et_2NLi\cdot 2Et_2NH \qquad (7)$$

In order to get a hint about the character of the lithium diethylamide—diethylamine complex, the addition reactions of some substituted styrene with the amide complex at$[Et_2NH]_0/[Et_2NLi]_0=10$ were studied. The first-order analyses and the rate constants are shown in Fig. 4. As is shown in Fig. 5, the resultant $\rho$ value is $+5.0$, in good agreement with the value reported for the anionic reaction system of polystyrylsodium with substituted styrene in tetrahydrofuran.[9)]

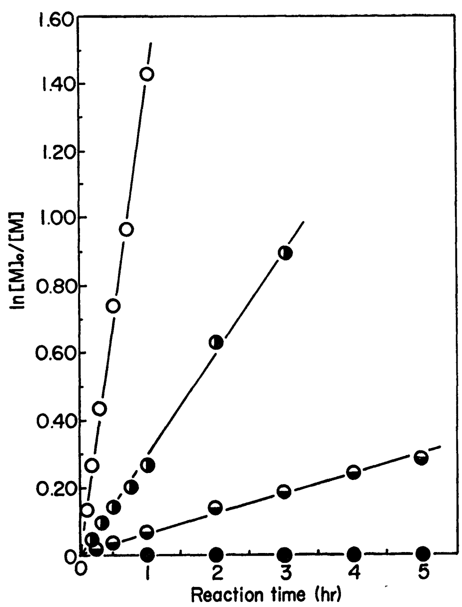

Fig. 4. First-order analyses of the reaction of $Et_2NH$-$Et_2NLi$ complex with substituted styrene.
$[Et_2NLi]_0=[\text{Styrene deriv.}]_0=0.250$ M, $[Et_2NH]_0/[Et_2NLi]_0=10$, in cyclohexane at 50 °C.
○ Styrene; ◑ *p*-methylstyrene; ⊖ *p*-methoxystyrene; ● α-methylstyrene.

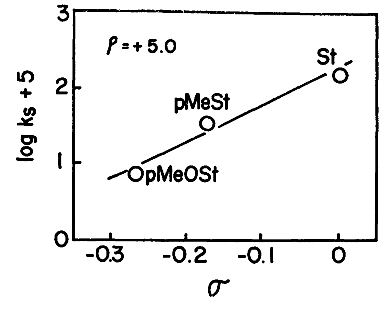

Fig. 5. Hammett $\sigma$-$\rho$ plot for *p*-substituted styrene with $Et_2NLi$-$Et_2NH$ complex.

TABLE 3. SECOND-ORDER RATE CONSTANTS OF ADDITION REACTION OF $Et_2NH$-$Et_2NLi$ COMPLEX WITH STYRENE AND BUTADIENE[a)]

| $\frac{[Et_2NH]_0}{[Et_2NLi]_0}$ | Styrene $k_S\times10^3$ l/mol·s | Butadiene $k_b\times10^3$ l/mol·s | Styrene-Butadiene | |
|---|---|---|---|---|
| | | | $k_S\times10^3$ l/mol·s | $k_b\times10^3$ l/mol·s |
| 3.0 | — | 0.85 | — | — |
| 10 | 1.6 | 1.4 | 1.5 | 1.6 |
| 15 | 2.0 | — | — | — |
| 28 | 2.6 | — | — | — |

a) In cyclohexane at 50°C. b) Ref. 2.

It is well known that, in the styrene–butadiene copolymerization with a lithium alkyl initiator in hydrocarbon media, the presence of a diene monomer pronouncedly suppresses the reactivity of styrene, although the rate of the homopolymerization of styrene is greater than that of butadiene under the same conditions. The microstructure of the butadiene units of the copolymer prepared under the above-mentioned copolymerization system is predominantly the 1,4-structure. On the other hand, when the reactivity of styrene is increased by the addition of some Lewis bases in the copolymerization system, the amount of the 1,2-structure in the butadiene units is also increased. In order to compare the reactivity of lithium diethylamide with that of lithium alkyl, the reactivity of styrene toward the lithium amide in the presence of butadiene was examined. It may be seen in Table 3 that the presence of butadiene has no effect on the reactivity of styrene in contrast with the reaction with lithium alkyl. Table 3 also shows the two monomers to possess rate constants of almost the same order of magnitude. The isomer

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[8)] R. J. Schlott, J. C. Falk, and K. W. Narducy, *J. Org. Chem.*, **37**, 4243 (1972).

[9)] M. Shima, D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **85**, 1306 (1963).

distribution of the 1-diethylaminobutene produced here is not different compared with the results reported previously.[2,3)

The above results suggest that the mechanism of the stereospecific addition reaction of the lithium diethylamide complex to butadiene is different from the usual stereospecific addition reaction of lithium alkyl in hydrocarbon solvents, since the 1,4-*cis*-structure formation in butadiene units is still retained, even under reaction conditions which result in comparable monomer reactivities in the styrene–butadiene copolymerization.