°C, $\mathrm{M^{-1}\,s^{-1}}$) decrease in the order RS^- (1.7×10^9) > OH^- (1.7×10^6) > RSH (1.2). Within a series of RS^- nucleophiles, basicity appears to be the prime determining factor, the stronger bases being more effective nucleophiles (see Figure 1). However, the most dramatic reactivity effect encountered in this work involves the relative rates of cleavage of coordinated and noncoorddinated disulfides. Table IX summarizes rate data for the reaction of organic disulfides with various nucleophiles, both with and without electrophilic assistance. For all relevant comparisons, the rate of reaction is much greater in the presence of an electrophile, but the effect induced by coordination of the disulfide to an inert cobalt(III) center is truly striking. From Table IX it is seen that coordination of a dialkyl disulfide to cobalt(III) enhances the rate of OH^- cleavage of the sulfur–sulfur bond by about 11 orders of magnitude and enhances the rate of RS^- cleavage by about 10 orders of magnitude. These very large effects reflect the inherent ability of the electrophilic cobalt(III) center to activate the disulfide linkage toward nucleophilic attack. It is just this sort of specific and effective activation of disulfide linkages that may be important in biological processes.

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Registry No. $[(en)_2Co(S(SCH_3)CH_2CH_2NH_2)]^{3+}$, 74037-02-8; $[(en)_2Co(S(SCH_2CH_3)CH_2CH_2NH_2)]^{3+}$, 74037-05-1; $[(en)_2Co(S(SCH(CH_3)_2)CH_2CH_2NH_2)]^{3+}$, 74037-00-6; $[(en)_2Co(S(SC(CH_3)_3)CH_2CH_2NH_2)]^{3+}$, 74036-99-0; $[(en)_2Co(S(SC(CH_3)_2CH(NH_2)COOH)CH_2CH_2NH_2)]^{3+}$, 84194-99-0; OH^-, 14280-30-9; 2-mercaptoethanol, 60-24-2; 3-mercaptopropionic acid, 107-96-0; 2-mercaptoethanesulfonic acid, 3375-50-6; cysteamine, 60-23-1; L-cysteine, 52-90-4; D-penicillamine, 52-67-5.

Supplementary Material Available: Table I, k_{obsd} and k_2 values for base hydrolysis reactions, Tables IV and V, k_{obsd} and k_2 values for thiol cleavage reactions (7 pages). Ordering information is given on any current masthead page.

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Kinetic Study for Reactions of Phenylseleno Radical with Vinyl Monomers

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Abstract: The reactivities of the phenylseleno radical (PhSe·) generated by flash photolysis of diphenyl diselenide have been determined. Low reactivities of PhSe· toward oxygen, hydrogen-atom donors, and halogen-atom donors have been confirmed. With vinyl monomers ($CH_2{=}CHY$) PhSe· reacts in a reversible fashion; by the addition of oxygen as a selective radical trap to the adduct radicals ($PhSeCH_2C{\cdot}HY$), the absolute addition rate constants have been determined. The reverse rate constants and the equilibrium constants have been estimated as relative ones from which the thermodynamic stabilities of the adduct radicals have been elucidated. The addition rates increase mainly with the stabilities of the adduct radicals and subsequently with the polar nature of the transition state. The lower reactivity of PhSe· compared with the phenylthio radical (PhS·) is attributed to the greater stabilization of an unpaired electron in PhSe· than that in PhS·.

Organoselenium compounds are useful for synthetic chemistry[1] and photochemistry.[2,3] Important reaction intermediates generated by photolysis of organoselenium compounds are the organoseleno radicals (RSe·);[4] the reaction products of the radical reactions with phosphines[5] and alkenes[6,7] have been identified. The reactivities of RSe·, however, have not been clarified compared with those of the organothio radicals.[8,9] We have shown that the flash photolysis technique is very valid in the kinetic study for the addition reactions of the phenylthio radical (PhS·) with vinyl monomers.[10,11] By the application of this technique to the free-radical addition reactions which are usually reversible, the relative equilibrium constants can be estimated by the addition of an appropriate selective radical trap; therefore, the reactivities of the free radicals can be discussed on the basis of the thermodynamic parameters. In this paper we applied the flash photolysis technique to the phenylseleno radical (PhSe·) in order to clarify the reactivities toward various substrates such as vinyl monomers. The results for PhSe· have been compared with those for PhS· observed previously by the same method.[10,11]

Results and Discussion

The transient absorption band (spectrum a in Figure 1) was observed at 490 nm by the flash photodecomposition of diphenyl diselenide (spectrum c in Figure 1) in carbon tetrachloride. The species of the 490-nm band was ascribed to PhSe· since a similar sharp absorption band was reported for *p*-methoxybenzeneseleno radical at 535 nm by means of pulse radiolysis;[12] such a shift of the absorption peaks between both the radicals is reasonable since

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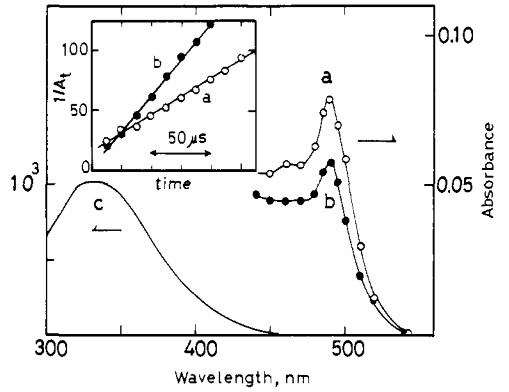

Figure 1. (a) Transient absorption spectrum of PhSe· generated by flash photodecomposition of PhSeSePh (8.7×10^{-4} M). (b) Spectrum of PhSe· observed in the presence of *m*-chlorostyrene (8.8×10^{-2} M) in carbon tetrachloride. Absorbance at 25 μs after each flash was depicted. (c) Spectrum of PhSeSePh. Insert: Second-order plots for the decay of PhSe· at 490 nm in a 10-cm optical cell; (a) in carbon tetrachloride and (b) in hexane at 23 ± 1 °C.

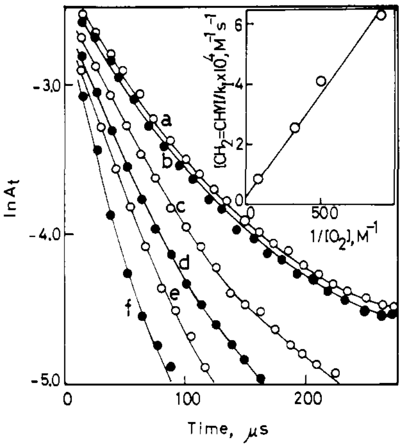

Figure 2. Oxygen effect on the first-order decay kinetics of PhSe· under a constant vinyl monomer concentration. [α-Methylstyrene]: (a) 0, (b–f) 3.1×10^{-2} M. [O_2]: (a,b) 0, (c) 1.0×10^{-3}, (d) 2.0×10^{-3}, (e) 3.1×10^{-3}, (f) 1.3×10^{-2} M. Insert: Plot of [CH_2=CHY]/k_I vs. 1/[O_2].

a similar shift has been observed in the cases of the phenylthio radical (490 nm) and the *p*-methoxybenzenethio radical (525 nm).[13,14]

Immediately after the flash, PhSe· begins decaying with second-order kinetics (insert of Figure 1), indicating that PhSe· decays predominantly with recombination (reaction 1). The slope of

$$\text{PhSeSePh} \underset{k_r}{\overset{h\nu}{\rightleftharpoons}} 2\text{PhSe}\cdot \qquad (1)$$

the second-order plot yields $2k_r/\epsilon$, where k_r and ϵ refer to the recombination rate constant and molar extinction coefficient of PhSe·, respectively. The low reactivity of PhSe· toward molecular oxygen was found since the decay profile was not changed significantly if the solution is oxygen saturated. Second-order kinetics was observed in halogen-atom donors or in hydrogen-atom donors (insert of Figure 1); this indicates that PhSe· is inactive to these substrates, which is similar to the low reactivity of PhS·.[10]

Since the $2k_r/\epsilon$ values depend upon the viscosity of solvents (insert of Figure 1), the k_r values are close to the diffusion-controlled limit. The k_r value can be calculated to be 7×10^9 M^{-1} s^{-1} in carbon tetrachloride from the Debye equation;[15] thus the ϵ value can be estimated to be 4700 M^{-1} cm^{-1} at 490 nm, from which the initial concentration of PhSe· generated by one flash exposure was estimated to be 2×10^{-6} M, using the initial absorbance of spectrum a in Figure 1. Since the k_r values calculated from the Debye equation are usually ~2–4 times larger than the values determined experimentally,[15] the ϵ value and the initial concentration of PhSe· estimated above may contain such an uncertainty.

Table 1. Rate Constants (k_1) and Relative Backward Rate Constants (k_{-1}/k_2) for the Addition Reactions of PhSe· with Vinyl Monomers in Carbon Tetrachloride at 23 ± 1 °C[a]

monomer[b]	Q	e	k_1, M^{-1} s^{-1}	k_{-1}/k_2, M
MSt	0.98	−1.27	2.9×10^6	2.0×10^{-2}
St	1.0	−0.8	2.2×10^6	3.1×10^{-2}
4VP	0.82	−0.20	5.0×10^5	1.3×10^{-2}
MMA	0.74	0.40	4.2×10^4	6.7×10^{-3}
MAN	1.12	0.81	2.7×10^4	7.6×10^{-3}
AN	0.60	1.20	1.4×10^4	1.8×10^{-2}
IBVE	0.023	−1.77	3.5×10^4	9.5×10^{-3}
EVE	0.032	−1.17	1.5×10^4	5.9×10^{-3}
VAc	0.026	−0.22	~10^3	

[a] Each rate constant contains the estimation error of ca. 20%. [b] Abbreviations of vinyl monomers: MSt, α-methylstyrene; St, styrene; 4VP, 4-vinylpyridine; MMA, methyl methacrylate; MAN, methacrylonitrile; AN, acrylonitrile; IBVE, isobutyl vinyl ether; EVE, ethyl vinyl ether; VAc, vinyl acetate.

By the addition of vinyl monomers such as α-methylstyrene to a degassed solution, the enhancement of the decay rate of PhSe· was not observed (Figure 2; decay curves a and b). When both monomer and oxygen were added, the decay rates increased and decay kinetics approached first order (curves c–f in Figure 2). The slopes of the first-order plots (k_I) increased with the O_2 concentration under a constant monomer concentration. When decay kinetics are mixed order, consisting of second order ($2k_r$[PhSe·]^2) and first order (k_I[PhSe·]), the k_I value can be estimated with a graphic[16] or computer simulation method[17] by the use of the $2k_r/\epsilon$ value previously estimated from the second-order plot. On the addition of both vinyl monomer and oxygen, the absorption spectrum was not altered (spectrum b in Figure 1); this suggests that the enhancement of the decay rates is attributed to the reaction of free PhSe· with monomer but not to the complex formation between them. From these findings it is presumed that the addition reaction of PhSe· with vinyl monomers is a reversible process and that oxygen acts as a selective radical trap to the adduct carbon-centered radicals (reaction 2). The similarity of

$$\text{PhSe}\cdot + CH_2{=}CHY \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{PhSeCH}_2\text{C}\cdot\text{HY} \xrightarrow[k_2]{O_2} \text{peroxy radical} \qquad (2)$$

decay curves a and b in Figure 2 indicates that the equilibrium is established during the flash duration of xenon lamp (ca. 10 μs). The reversibility of the addition reaction of RSe· with vinyl monomers has been presumed by Brown, Cross, and Millington in the product analysis experiment[5] and by Scaiano and Ingold in the ESR measurements.[6] The anti-Markovnikov addition products were isolated by Russell and Hershberger.[7] These phenomena in the flash photolysis are similar to those for the reversible addition of PhS· which were first observed by us[10] and lately confirmed by Natarajan, Lembke, and Kuntz,[18]

In rate expression 3 for reactions 1 and 2, the concentration

$$-d[\text{PhSe}\cdot]/dt = 2k_r[\text{PhSe}\cdot]^2 + k_1[\text{PhSe}\cdot][CH_2{=}CHY] - k_{-1}[\text{PhSeCH}_2\text{C}\cdot\text{HY}] \qquad (3)$$

of $PhSeCH_2C{\cdot}HY$ may be approximated by a steady-state assumption; thus we can derive eq 4 where k_I refers to the first-order

$$k_I = k_1[1 - k_{-1}/(k_{-1} + k_2[O_2])][CH_2{=}CHY] \qquad (4)$$

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Table II. Rate Constants (k_1) and Relative Backward Rate Constants (k_{-1}/k_2) for the Addition Reactions of PhSe· with Substituted Styrenes in Carbon Tetrachloride at 23 ± 1 °C[a]

substituent	k_1, M^{-1} s^{-1}	k_{-1}/k_2, M
m-Cl	1.7×10^6	1.1×10^{-2}
p-Br	1.9×10^6	2.2×10^{-2}
p-Cl	1.8×10^6	1.8×10^{-2}
m-CH_3	2.5×10^6	3.5×10^{-2}
p-CH_3	3.3×10^6	2.0×10^{-2}
p-CH_3O	5.0×10^6	4.8×10^{-2}

[a] Each rate constant contains the estimation error of ca. 20%.

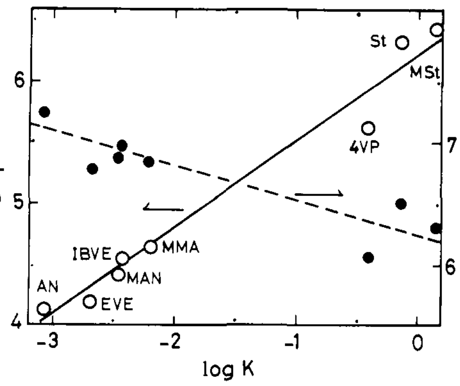

Figure 3. Plots for the linear free energy relationship: (○) log k_1 vs. log K and (●) log k_{-1} vs. log K. For the assumption of the k_2 values, see text. Abbreviations of vinyl monomers are shown in Table I.

rate constant observed in a large excess of vinyl monomer (>10^{-2} M) under a constant oxygen concentration (~10^{-3}–10^{-2} M). Equation 5 can be derived from the reciprocal of eq 4.

$$[CH_2{=}CHY]/k_I = 1/k_1 + k_{-1}/k_1k_2[O_2] \quad (5)$$

Insert of Figure 2 shows the plots of $[CH_2{=}CHY]/k_I$ vs. $1/[O_2]$ for the case of α-methylstyrene; a linear correlation was observed. Similar correlations were observed for other vinyl monomers. The k_1 values were directly estimated from the intercepts and the k_{-1}/k_2 values were estimated from the slopes. The k_1 and k_{-1}/k_2 values are summarized in Table I for conjugated and nonconjugated vinyl monomers and those for meta- and para-substituted styrenes in Table II. In the case of vinyl acetate the $k_I/[CH_2{=}CHY]$ value in the oxygen-saturated solution was assumed to equal k_1 since the oxygen effect was small. Replacing the k_2 value by the reported one (~10^8–10^9 M^{-1} s^{-1}),[19,20] we can estimate the k_{-1} values to be ~10^6–10^7 s^{-1} from tables. These values suggest that the backward reactions are considerably fast and that the equilibrium would be established during the flash duration of the xenon lamp (ca. 10 μs). The equilibrium constant K ($=k_1/k_{-1}$), which can be obtained in the form of Kk_2, can be similarly estimated to be ~1–10^{-3} M^{-1}; this indicates the endothermic addition reaction.

Since log K values are a measure of the thermodynamic stabilities of $PhSeCH_2C{\cdot}HY$, the linear free energy relationship can be investigated by plotting the log k_1 or log k_{-1} values against the log K values (Figure 3), in which $k_2 = 10^8$ M^{-1} s^{-1} is assumed for α-methylstyrene, styrene, and 4-vinylpyridine and $k_2 = 10^9$ M^{-1} s^{-1} for other vinyl monomers.[19,20] The slopes of 0.70 for log k_1 and −0.30 for log k_{-1} in Figure 3 can be assigned to the α and β values in eq 6 and 7, respectively.[21] These values are compatible

$$\Delta \log k_1 = \alpha \Delta \log K \quad (6)$$

$$\Delta \log k_{-1} = -\beta \Delta \log K \quad (7)$$

with Semenov's empirical values for the endothermic ($\alpha = 0.75$) and exothermic radical reactions ($\beta = 0.25$).[22] This finding suggests that a main factor controlling the rates of both the forward and backward reactions is the stability of $PhSeCH_2C{\cdot}HY$.

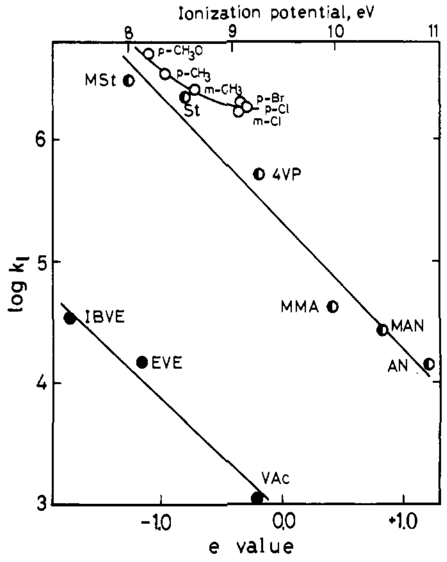

Figure 4. Plots of log k_1 vs. *e* values (or ionization potentials): (○) substituted styrenes; (◐) conjugated vinyl monomers; (●) nonconjugated vinyl monomers. The ionization potentials of nonconjugated vinyl monomers are estimated by adding about 1 eV to the abscissa.

The linear free energy relationship examined above does not always contradict other factors controlling the reactivities, since the linear correlations in Figure 3 are based on the rough assumption of the k_2 values. The polar effect was found in the plots of log k_1 vs. the polarity parameters of vinyl monomers such as the *e* value and ionization potential (Figure 4).[23-26] The points can be classified into three groups: substituted styrenes, conjugated vinyl monomers, and nonconjugated ones. The importance of the stabilities of the adduct radicals is again apparent since the group of conjugated vinyl monomers is above that of nonconjugated ones. The negative slope of each group indicates that the addition rates of PhSe· with vinyl monomers are enhanced with an increase in the electron density of the double bond. In general, such an effect can be attributed to the polar transition state (e.g. $[PhSe^-, CH_2{=}CHY^{+}\cdot]$).[27-30] In our case, however, considerable part of the negative slopes in Figure 4 may be ascribed to the polar effect on the stabilities of $PhSeCH_2C{\cdot}HY$ as the linear free energy relationship suggests; therefore, remaining part is attributed to the polar transition state.

The Hammett plot of log k_1 for substituted styrenes vs. σ shows a similar curve to that in Figure 4 since the *e* values (or ionization potential) are linearly correlated with σ.[31] A line, however, was obtained in the plot vs. σ^+, which yields $\rho^+ = -0.50 \pm 0.10$. A similar tendency was found for the plot of log k_{-1}/k_2 vs. σ^+, which indicates the polar effect on the common transition state. The negative ρ^+ value can be interpreted by the partial electron shift

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from the double bond of the vinyl monomer to the radical center of PhSe·.

The addition rate constant of PhSe· for each vinyl monomer is smaller than that of PhS· by a factor of ~10–50.[11,32] The lower reactivity of PhSe· is mainly attributed to the thermodynamic stability of PhSe· since the Kk_2 value for PhSe· is smaller than that of PhS·.[11,32] The ρ^+ value of PhSe· for substituted styrenes (−0.50) is more negative than that of PhS· (−0.26);[33] the polar nature of the transition state for PhSe· is greater than that of PhS·. The contribution of the polar effect to the actual rate, however, does not surpass that of the thermodynamic stability in the reactant.

Our findings for the reactivities of PhSe· and PhS· are compatible with the fact that the Se atom is less reactive than the S atom in the addition reaction with alkenes.[34] The polarization in the transition state of the Se atom addition reaction is presumed by Callear and Tyerman.[35] The bond dissociation energy data suggest that the selenium-centered radicals are in general more stable than the sulfur-centered radicals.[36]

Experimental Section

Commercially available diphenyl diselenide was purified by recrystallization. Vinyl monomers were used after distillation at reduced pressure. Carbon tetrachloride and hexane used as solvents were of spectrophotometric grade.

The flash experiments were made at room temperature controlled at 23 ± 1 °C. The flash apparatus was of standard design; half-duration and flash energy of xenon flash lamps (Xenon Corp. N-851 C) were ca. 10 μs and 150 J, respectively. The flash light in the range of 350–450 nm was selected by the use of appropriate light filters. Kinetic observations were made with a continuous monitor light source and photomultiplier detection. The oxygen concentrations of solutions were calculated from Henry's law by dissolving oxygen under partial pressure.[37]

Acknowledgment. I thank Professor M. Matsuda and Dr. M. Miyashita of Tohoku University for many helpful suggestions during the course of this study.

Registry No. Phenylseleno radical, 84065-55-4; α-methylstyrene, 98-83-9; styrene, 100-42-5; 4-vinylpyridine, 100-43-6; methyl methacrylate, 80-62-6; methacrylonitrile, 126-98-7; acrylonitrile, 107-13-1; isobutyl vinyl ether, 109-53-5; ethyl vinyl ether, 109-92-2; vinyl acetate, 108-05-4; *m*-chlorostyrene, 2039-85-2; *p*-bromostyrene, 2039-82-9; *p*-chlorostyrene, 1073-67-2; *m*-methylstyrene, 100-80-1; *p*-methylstyrene, 622-97-9; *p*-methoxystyrene, 637-69-4.

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Enlarged Deuterium Isotope Effects in Oxyanion-Catalyzed 1,3 Proton Transfer Competing with 1,2 Elimination as a Probe of a Common Tightly Hydrogen-Bonded Intermediate

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Contribution from the Institute of Chemistry, University of Uppsala, P.O. Box 531, S-751 21 Uppsala, Sweden. *Received June 14, 1982*

Abstract: The reaction of 1-(2-acetoxy-2-propyl)indene (**1**-h) or 1-(2-acetoxy-2-propyl)[1,3-$^2H_2$]indene (**1**-d) with *p*-NO_2PhO^- in methanol buffered with *p*-NO_2PhOH results in base-catalyzed 1,3 proton transfer, yielding 3-(2-acetoxy-2-propyl)indene (**2**-h) and 3-(2-acetoxy-2-propyl)[1,1-$^2H_2$]indene (**2**-d), respectively, in competition with base-promoted 1,2 elimination producing 1-isopropylideneindene (**3**-h) and 1-isopropylidene[3-^{2}H]indene (**3**-d), respectively. The overall deuterium isotope effect on the reaction of **1** was measured as $(k_{12}{}^H + k_{13}{}^H)/(k_{12}{}^D + k_{13}{}^D) = 5.2$, which is composed of the rearrangement isotope effect $k_{12}{}^H/k_{12}{}^D = 12.2 \pm 1.0$ and the elimination isotope effect $k_{13}{}^H/k_{13}{}^D = 3.6$. The enlarged rearrangement isotope effect shows that the intramolecularity of the 1,3 proton-transfer reaction is substantial. The intramolecularity was determined as ca. 87% for [*p*-NO_2PhOH] = 0.24 M and ca. 80% for [*p*-NO_2PhOH] = 0.71 M by analyzing the ^{2}H content of the product **2**-d. The amplified isotope effect on the 1,3-prototropic shift together with the attenuated elimination isotope effect shows that the two reactions are coupled via at least one common intermediate, which is concluded to be a tightly hydrogen-bonded complex between the protonated base and the carbanion. An increase in basicity of the oxyanion favors elimination at the expense of rearrangement. Reaction of **2**-h and **2**-d predominantly give 1,4 elimination accompanied by a trace of competing 1,3 proton transfer. The isotope effect $k_{23}{}^H/k_{23}{}^D$ was measured to 2.5; it is small owing to a large amount of internal return.

Tightly hydrogen-bonded carbanions are rather well-known intermediates in proton-transfer reactions, at least in nonpolar solvents.[1] A hydrogen-bonded complex between the conjugate acid of the proton-abstracting base and the carbanion is formed in the reaction. This intermediate can directly provide product (which, for example, may be a tautomer), initially undergo hydrogen exchange with the solvent or another hydrogen pool, or dissociate to a solvent-equilibrated carbanion. The latter behavior was found by Cram and co-workers when studying the 1,3 deuteron transfer of (−)-3-*tert*-butyl-1-methyl[1-^{2}H]indene in MeOK/MeOH.[2] The reaction was found to be <0.5% intramolecular and gives racemic product. Similarly, Ahlberg reported that 1-(2-hydroxy-2-propyl)indene rearranges intermolecularly in MeOK/MeOD.[3]

An increase in the collapse rate relative to dissociation of the initially formed intermediate, i.e., an increase in the intramo-

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