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Effect of Pressure on [2]Pseudorotaxane Formation and Decomplexation and Their Corresponding Activation Volumes

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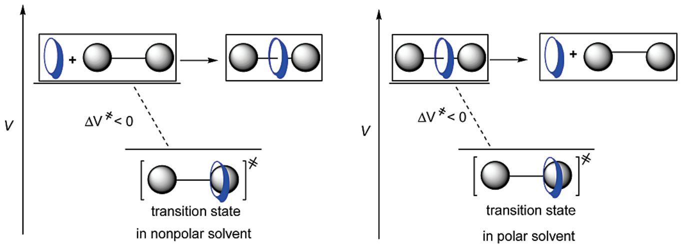

In this study, we investigated the effect of pressure on the formation and decomplexation of [2]pseudorotaxanes. High pressure accelerated the formation of [2]pseudorotaxanes in an aprotic nonpolar solvent ($CDCl_3/CD_3CN$) via the slipping approach when using two crown ether/secondary ammonium salt systems: dibenzo[24]crown-8/bis(cyclohexylmethyl)ammonium salt (**1a/2a**) and tetrabenzo[24]crown-8/dibenzylammonium salt (**1b/2b**). The influence of pressure on the rate constants for the formation of the [2]pseudorotaxanes **3a** and **3b** revealed activation volumes ($\Delta V^{\ddagger}$) of −2.5 and −4.6 cm^3 mol^{-1}, respectively, at 303 K and zero pressure. We also investigated the effect of pressure on the decomplexation of the [2]pseudorotaxanes **3a** and **3b** in a polar solvent (DMSO-d_6/$CDCl_3$), obtaining activation volumes of −0.9 and −0.4 cm^3 mol^{-1}, respectively, at 303 K and zero pressure. Moreover, we calculated the activation parameters for the decomplexation processes on the basis of transition state theory at each pressure.

Introduction

Noncovalent interactions are routinely exploited in receptors designed to coordinate organic and inorganic species; they also play critical roles in restricting molecular dynamics.[1] Catenanes and rotaxanes that contain two or more recognition sites in one of their components can exist as two or more different translational isomers.[2] Regulating the motion of these isomers, or the association and dissociation

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of pseudorotaxanes, in response to external stimuli is an attractive challenge because such switching systems would aid the development of molecular sensors,[3] functionalized surfaces,[3e,4] nanovalves,[5] and drug delivery systems.[6,7] Many molecular switch systems based on rotaxane structures respond to external stimuli, including light,[8] electrochemical reduction and oxidation,[8b,9] temperature,[10] pH,[9a,11] solvent polarity,[12] and chemical additives.[11k,13] In real device applications, it would probably be more preferable to use physical external stimuli, rather than internal chemical stimuli, to perform repeated reversible molecular switching to avoid any build-up of unwanted chemical species.

Pressure is a fundamental physical stimulus that influences thermodynamic and kinetic parameters. Studies of pressure-dependent reactions reveal information on the volume change during the process, akin to studies of temperature-dependent reactions to obtain the energy of the process.[14] For any reaction in solution, the reaction volume ΔV is defined as the volume difference between the substrate(s) and product(s), and the activation volume $\Delta V^{\ddagger}$ is equal to the value obtained after subtracting the volume of the transition

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state from the total volume of the substrate(s). The relationship between ΔV (or $\Delta V^{\ddagger}$) and the pressure dependence of the equilibrium (or rate) constant originates from the fundamental thermodynamic equations. The equilibrium of a reversible chemical reaction is affected by the applied pressure, as described using the well-known eq 1

$$\mathrm{d}\ln K/\mathrm{d}P = -\Delta V/RT \tag{1}$$

where K represents the equilibrium constant, T and P are the system's absolute temperature and pressure, and R is the universal gas constant.

Furthermore, a reaction proceeding via a transition state possessing a highly negative activation volume is significantly accelerated under high-pressure conditions. Many examples of this phenomenon have been reported for reactions in which the molecularity decreases along the reaction coordinate, such as cycloadditions and condensations.[14] The relationship between the rate constant k and pressure is given by

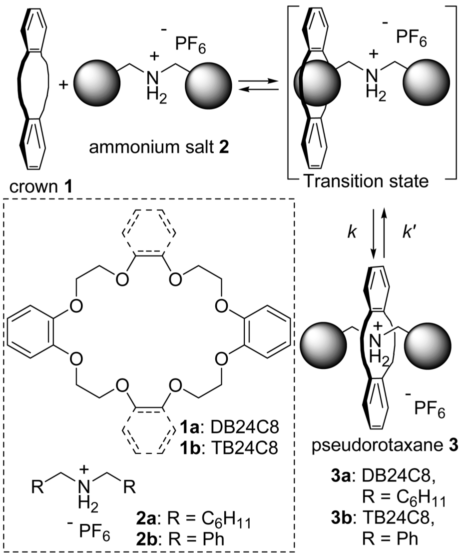
$$\mathrm{d}\ln k/\mathrm{d}P = -\Delta V^{\ddagger}/RT \tag{2}$$

Therefore, the application of high pressure to a reaction mixture containing self-assembled molecules can be used as an external stimulus to control their molecular dynamics kinetically and thermodynamically. Furthermore, the kinetic and thermodynamic effects of pressure on supramolecular complexation can be quantified in terms of reaction and activation volumes. Herein, we describe the effects of pressure on thermal [2]pseudorotaxane formation, from secondary ammonium ions and crown ethers, using the slipping method; we provide detailed kinetic data regarding the enhancement of [2]pseudorotaxane formation and decomplexation under various applied pressures.[15,16]

Results and Discussion

Formation of [2]Pseudorotaxanes at Ambient Pressure. The formation of 1:1 complexes from [24]crown-8 derivatives and secondary ammonium ions in solution is well-established.[17] Indeed, the formation of [2]pseudorotaxanes from the crown ethers **1a** and **1b** and the ammonium ions **2a** and **2b**, respectively, proceeds slowly at ambient pressure and temperature (Scheme 1).[18,19] For our present studies, we chose $CDCl_3/CD_3CN$ (1:1) as the reaction solvent. ^1H NMR spectra of 50 mM solutions of the host and guest components **1a** and **2a**, respectively, were recorded at 303 K. We confirmed the formation of the [2]pseudorotaxane **3a** by comparing the ^1H NMR spectrum of the mixture with that described previously;[18] integrations of the intensities of various signals afforded the concentrations of the three species (i.e., host, guest, and complex). Plotting 1/[**2a**] with respect to time provided a straight line at low conversion (Figure S1, Supporting Information).[20,21] The transformation closely resembled a second-order reaction; therefore, the reverse process could be ignored until the [2]pseudorotaxane formation reached 10% conversion.

SCHEME 1. Thermal Formation of a [2]Pseudorotaxane via Slipping



Effect of Pressure on [2]Pseudorotaxane Formation. A solution of the crown ether **1a** (15 mM) and the ammonium salt **2a** (15 mM) in $CDCl_3/CD_3CN$ (1:1) was subjected to a pressure of 200 MPa at 303 K and the extent of [2]pseudorotaxane formation was monitored at low conversion (< 10%) with ^1H NMR spectroscopy. The second-order plots for the complexation of **1a** and **2a** reveal that high pressure accelerated the [2]pseudorotaxane formation relative to that under ambient conditions. In the same manner, we subjected equimolar mixtures of the two components to pressures ranging from 250 to 500 MPa. In each case, the plot of 1/[**2a**] with respect to time at low conversion could be fit to a straight line, the slope of which afforded the second-order rate constant k,[20] which was affected by the applied pressure (Figure S2, Supporting Information).[21] We also performed these [2]pseudorotaxane formation processes in the same manner at 313, 323, and 333 K; we found that the complexation was accelerated upon increasing the applied pressure and temperature (Figures S3−5, Supporting Information).[21]

Next, we used tetrabenzo[24]crown-8 (**1b**) and dibenzylammonium hexafluorophosphate (**2b**) as substrates to investigate the effects of pressure on the reaction rate. We employed a 10 mM mixture of both reactants in $CDCl_3/CD_3CN$ (2:1), in consideration of the reaction rate and the solubilities of the crown ether **1b** and the resulting

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[15] Part of this study has been published as a preliminary communication: Tokunaga, Y.; Wakamatsu, N.; Ohbayashi, A.; Akasaka, K.; Saeki, S.; Hisada, K.; Goda, T.; Shimomura, Y. *Tetrahedron Lett.* **2006**, *47*, 2679–2682.

[16] The molar volumes of a catenane and its non-interlocked rings have been discussed in terms of measurement of their densities; see: Morel-Desrosiers, N.; Morel, J.-P.; Dietrich-Buchecker, C. O.; Weiss, J.; Sauvage, J.-P. *New J. Chem.* **1988**, *12*, 205–208.

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[18] For the pairing of **1a** and **2a**, see: Ashton, P. R.; Baxter, I.; Fyfe, M. C. T.; Raymo, F. M.; Spencer, N.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 2297–2307.

[19] For the pairing of **2a** and **2b**, see: Tokunaga, Y.; Goda, T.; Wakamatsu, N.; Nakata, R.; Shimomura, Y. *Heterocycles* **2006**, *68*, 5–10.

[20] The second-order rate equation would be next:

$$-\mathrm{d}[\mathbf{1a}]/\mathrm{d}t = -\mathrm{d}[\mathbf{2a}]/\mathrm{d}t = k[\mathbf{1a}][\mathbf{2a}]$$

In the case of $[\mathbf{1a}]_0 = [\mathbf{2a}]_0$:

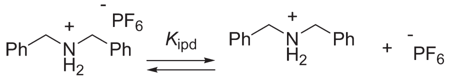
$$1/[\mathbf{2a}] = kt + 1/[\mathbf{2a}]_0$$

[21] See the Supporting Information.

[2]pseudorotaxane **3b**. Again, we observed enhancements in the rate of [2]pseudorotaxane formation upon increasing the applied pressure from 0.1 to 350 MPa and the temperature from 303 to 333 K; the results were similar to those for the complexation of **1a** and **2a** (Figures S6–9, Supporting Information).[21]

In general, reactions in which the molecularity decreases upon proceeding from reactants to products have negative activation volumes. Indeed, the activation volume for rotaxane formation via the slipping method, in which the molecularity decreases, is negative.

Gibson reported that ion pairing of the ammonium salt **2a** affects the formation of [2]pseudorotaxanes derived from ammonium ion/crown ether pairs; thus, determination of the experimental association constant for [2]pseudorotaxane formation must take ion pair decomplexation (ipd) into consideration as a pre-equilibrium step [eq 3].[22,23]



2a **2a**$^+$

$$K_{ipd} = \frac{[\mathbf{2a}^+][PF_6^-]}{[\mathbf{2a}\text{-}PF_6]} \qquad (3)$$

Ion pairing has two considerable effects during pseudorotaxane formation. The first is a change in the concentrations of ammonium ions and salt ($\mathbf{2a}^+$ and **2a**) during the complexation process. According to Gibson, the value of K_{ipd} for **2a** in $CDCl_3/CD_3CN$ (3:2) at 295 K is 2.6×10^{-2} M. This value suggests that the ionic form of $\mathbf{2a}^+$ comprises ca. 80% of the ammonium species present in solution at 295 K and ambient pressure; additionally, this percentage would barely change at conversions of less than 10%. The second effect of ion pairing is its pressure dependence. Eckert reported the effects of pressure on the ionic associations of several ammonium salts in aprotic polar solvents, such as acetone and acetonitrile,[24] finding that the ion pairing association constants decrease upon increasing pressure in the range from 0.1 to ca. 200 MPa. Even though high pressure would accelerate the decomplexation of the ion pairs of the ammonium salts **2**, the maximum enhancement in the rate of pseudorotaxane formation would be ca. 1.25-fold, because ca. 80% of the ammonium species already exist in ionic form at ambient pressure.[25]

Activation Volumes for [2]Pseudorotaxane Formation. We determined rate constants for [2]pseudorotaxane formation from **1** and **2** via the slipping method in solution at various temperatures and pressures. The activation volumes at zero pressure were determined from a least-squares fit of the rate constants to eq 4,[14] using data obtained with eq 2 at pressures of up to 450–500 MPa for **1** and 300–350 MPa for **2** at each temperature.

$$\ln k = aP^2 + bP + c \qquad (4)$$

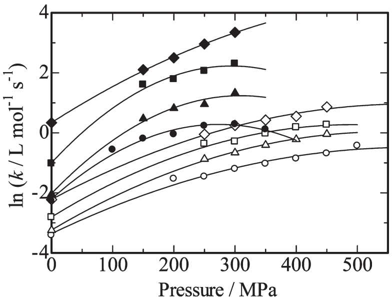


FIGURE 1. Plots of ln *k*, measured for the formation of the [2]pseudorotaxanes **3a** and **3b**, plotted as a function of pressure; solid lines are best fits for the data based on eq 4. **1a**/**2a**: (○) 303, (△) 313, (□) 323, and (◇) 333 K. **1b**/**2b**: (●) 303, (▲) 313, (■) 323, and (◆) 333 K.

TABLE 1. Temperature Dependence of the Activation Volumes for the Complexation of 1 and 2 at Zero Pressure

temp [K]	**1a**–**2a** [cm^3 mol^{-1}]	**1b**–**2b** [cm^3 mol^{-1}]
303	−2.5	−4.6
313	−3.1	−5.5
323	−3.4	−5.9
333	−3.2	−3.6

Figure 1 presents the plots of ln *k* with respect to pressure; Table 1 lists the activation volumes of the complexation processes at each temperature.[26] We estimated the activation volumes for formation of the [2]pseudorotaxanes **3a** and **3b** to be −2.5 and −4.6 cm^3 mol^{-1}, respectively, at zero pressure and 303 K. Although not as strongly negative as those of typical reactions in which the molecularity decreases during the process, large negative activation volumes usually exist for transition states in which a covalent bond is formed; for example, simple radical decompositions generally have activation volumes of ca. +10 cm^3 mol^{-1}.[14a,e] Despite the absence of covalent bond formation in the complexation events leading to pseudorotaxane creation, these processes presumably exhibit negative activation volumes because the passage of the stopper groups through the cavities of the crown ethers is the rate limiting step.

Interestingly, [2]pseudorotaxane formation from **1b** and **2b**, which contain a larger number of rigid benzene rings, exhibited a more negative activation volume than that from **1a**/**2a**. We suspect that two factors might be responsible for this phenomenon: (1) the rigid aromatic units of both substrates **1b** and **2b** undergo stacking to form a more compact transition state and (2) differences in the degrees of solvation of the substrates **1a**/**2a** and **1b**/**2b** and/or their transition states.

Effect of Pressure on the Decomplexation of the [2]Pseudorotaxanes. The decomplexation of [2]pseudorotaxanes formed from ammonium salts and crown ethers resembles a first-order reaction,[27] with polar solvents accelerating the

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(22) Jones, J. W.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, *125*, 7001–7004.

(23) The importance of ion pairing on the association of ammonium ions with crown ethers has also been reported previously; see: Montalti, M. *Chem. Commun.* **1998**, 1461–1462.

(24) (a) Glugla, P. G.; Byon, J. H.; Eckert, C. A. *J. Chem. Eng. Data* **1981**, *26*, 80–84. See also: (b) Everaert, J.; Persoons, A. *J. Phys. Chem.* **1982**, *86*, 546–552 and references cited therein.

(25) We did not estimate the association constants (K_{ipd}) for the ion pairing of the ammonium salts **2** in our solvents at various temperatures and pressures. All of the reported values are those obtained when ion pairing is ignored.

(26) The activation volumes of the complexation processes were already reported.[15] The difference of the values between previous studies and this report is due to the addition of another experiment and disparity in pressures.

(27) (a) Chiu, S.-H.; Rowan, S. J.; Cantrill, S. J.; Glink, P. T.; Garrell, R. L.; Stoddart, J. F. *Org. Lett.* **2000**, *2*, 3631–3634. (b) Tachibana, Y.; Kihara, N.; Furusho, Y.; Takata, T. *Org. Lett.* **2004**, *6*, 4507–4509. (c) Tokunaga, Y.; Akasaka, K.; Hashimoto, N.; Yamanaka, S.; Hisada, K.; Shimomura, Y.; Kakuchi, S. *J. Org. Chem.* **2009**, *74*, 2374–2379.

process by weakening the hydrogen bonds between the ammonium ion and the crown ether. For example, Stoddart reported that the [2]pseudorotaxane **3a** dissociated completely in less than 18 h at ambient temperature and pressure when dissolved in DMSO-d_6.[27a] We used ^{1}H NMR spectroscopy to monitor the decomplexation of **3a** (5 mM) in $CDCl_3$/DMSO-d_6 (1:1) at 303 K and atmospheric pressure. The plot of the concentration of the [2]pseudorotaxane **3a** provided a first-order curve; we obtained the decomplexation rate constant k' from the slope of the straight line of the plot of ln ($[\mathbf{3a}]_t/[\mathbf{3a}]_0$) against time ($t$), where $[\mathbf{3a}]_0$ and $[\mathbf{3a}]_t$ are the initial concentration of **3a** and that at time t, respectively; the half-life ($\tau_{1/2}$) of **3a** was 14.6 h. Using the same approach, we determined the value of $\tau_{1/2}$ (303 K, 0.1 MPa) for **3b** (2 mM) in $CDCl_3$/DMSO-d_6 (2:1) to be 12.3 h.[28] Next, we investigated the effect of pressure on the decomplexation of the [2]pseudorotaxanes **3a** and **3b**. We monitored these decomplexation processes using a 5 mM solution of **3a** in $CDCl_3$/DMSO-d_6 (1:1) and a 2 mM solution of **3b** in $CDCl_3$/DMSO-d_6 (2:1) at temperatures from 303 to 333 K and pressures ranging up to 500 and 300 MPa, respectively. All of the processes exhibited typical first-order behavior, with higher pressure accelerating the decomplexation of the [2]pseudorotaxanes **3** (Figure 2).[21]

Activation Volumes for the Decomplexation of the [2]-Pseudorotaxanes. The plots of ln k' with respect to pressure for the decomplexation of the [2]pseudorotaxanes **3** are nonlinear (Figure 3). We determined the activation volumes at 0 MPa from a least-squares fit of the data to eqs 2 and 4, using data obtained at pressures of up to 300−500 MPa for **3a** and 300 MPa for **3b** at each temperature. Interestingly, the calculated activation volumes ($\Delta V^{\ddagger}$) for these two decomplexation processes are also negative at zero pressure and 303 K: -0.9 cm^3 mol^{-1} for **3a** and -0.4 cm^3 mol^{-1} for **3b** (Table 2). Negative or positive activation volumes are mainly observed for organic reactions involving covalent bond formation or cleavage; notably, however, no covalent bonds are formed or cleaved during the decomplexation of these [2]pseudorotaxanes. Because the substrates **3** have compact structures, because of strong hydrogen bonding between the ammonium ions and the crown ethers, we suspect that the negative activation volumes for these decomplexation processes arise from (1) the complementary sizes of the cavities of the crown ethers and the stopper units, similar to those during [2]pseudorotaxane formation, and (2) the compression of the molecules, caused by electrostatic interactions with the polar solvent;[29] note that ion pairing decreases upon increasing the pressure in polar solvents, as described above.[24] In the [2]pseudorotaxanes, the ammonium ion moieties are encapsulated by the crown ether units; in contrast, these moieties interact electrostatically with polar solvents in the transition states, resulting in volume changes.[30]

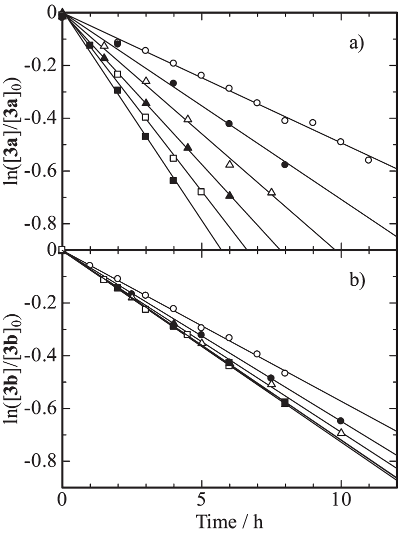

FIGURE 2. (a) First-order plots of ln ($[\mathbf{3a}]/[\mathbf{3a}]_0$) with respect to time for the decomplexation of **3a** (5 mM) in $CDCl_3$/DMSO-d_6 (1:1) at 303 K. (b) First-order plots of ln ($[\mathbf{3b}]/[\mathbf{3b}]_0$) with respect to time for the decomplexation of **3b** (2 mM) in $CDCl_3$/DMSO-d_6 (2:1) at 303 K. Pressure: (○) 0.1, (●) 100, (△) 200, (▲) 300, (□) 400, and (■) 500 MPa.

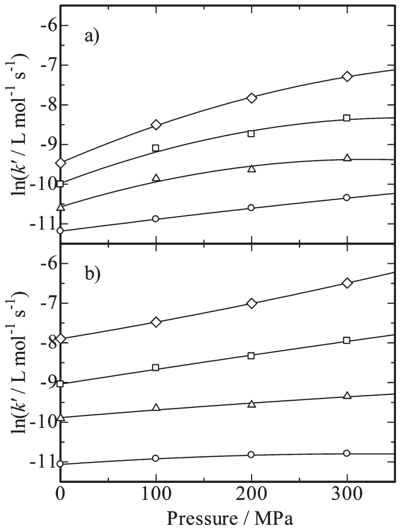

FIGURE 3. Pressure dependence of ln k' for the decomplexation of the [2]pseudorotaxanes (a) **3a** (5 mM) in $CDCl_3$/DMSO-d_6 (1:1) and (b) **3b** (2 mM) in $CDCl_3$/DMSO-d_6 (2:1) at (○) 303, (△) 313, (□) 323, and (◇) 333 K; solid lines are best fits for the data based on eq 4.

Effect of Pressure on the Kinetic Parameters for the Decomplexation of [2]Pseudorotaxanes. Because we determined the rate constants for [2]pseudorotaxane decomplexation at various temperatures and pressures, we could calculate the kinetic parameters associated with these systems at each pressure based on transition state theory. Eyring plots of the data for the [2]pseudorotaxane decomplexation processes yielded straight lines (Figure 4a,b); Table 3 lists the corresponding kinetic parameters. The activation free energies ($\Delta G^{\ddagger}$) were similar at each pressure; the activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) increased upon increasing the pressure.

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(28) The concentrations of the two substrates are different because of the low solubility of the [2]pseudorotaxane **3b** in a mixture of $CDCl_3$ and DMSO-d_6.

(29) Whalley, E. *J. Chem. Phys.* **1963**, *38*, 1400–1405.

(30) Merbach groups reported volume profiles for complexation of α-cyclodextrin with diphenyl azo dyes using high-pressure kinetic experiments. The complexation consists of two processes, and generally the activation volumes of both processes were more negative than those of the pseudorotaxane formation; see: Abou-Hamdan, A.; Bugnon, P.; Saudan, C.; Lye, P. G.; Merbach, A. E. *J. Am. Chem. Soc.* **2000**, *122*, 592–602.

TABLE 2. Temperature Dependence of the Activation Volumes for [2]Pseudorotaxane Decomplexation at Zero Pressure

temp [K]	**3a** [cm^3 mol^{-1}]	**3b** [cm^3 mol^{-1}]
303	−0.9	−0.4
313	−1.9	−0.5
323	−2.4	−0.9
333	−2.8	−0.9

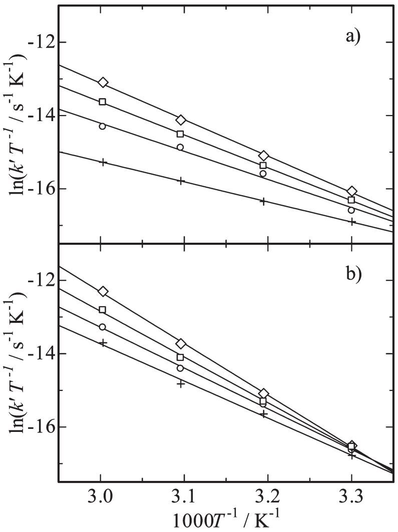

FIGURE 4. Eyring plots for the decomplexation of the [2]pseudorotaxanes (a) **3a** (5 mM) in $CDCl_3$/DMSO-d_6 (1:1) and (b) **3b** (2 mM) in $CDCl_3$/DMSO-d_6 (2:1) at (+) 0.1, (○) 100, (□) 200, and (◇) 300 MPa.

Although the activation free energies of **3a** and **3b** were almost identical, the activation enthalpy and entropy of **3a** were both smaller than those of **3b**. The entropic destabilization of the transition state for the decomplexation of **3a** became an enthalpic one upon increasing the pressure. In the decomplexation of **3b**, enthalpy contributed to the destabilization of the transition state, even at ambient pressure. We suspect that because the [2]pseudorotaxane **3b** possesses six rigid benzene rings, which fix the conformation in the ground state, its loss of conformational freedom in the transition state is relatively small.[31]

Figure 5 presents $T\Delta S^\ddagger$ plotted against $\Delta H^\ddagger$. We obtained straight lines having slopes (**3a**: 1.05; **3b**: 1.02) representing the extent to which the enthalpic gain was canceled by the accompanying entropic loss; the intercepts (**3a**: −105 kJ mol^{-1}; **3b**: −104 kJ mol^{-1}) represent the complex stabilities obtained at a value of $\Delta H^\ddagger$ of 0. The good relationships between $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ suggest that the decomplexation mechanisms were independent of the pressure and occurred with similar kinetic processes.

TABLE 3. Kinetic Data for the Decomplexation of the [2]Pseudorotaxanes (a) 3a and (b) 3b at Various Pressures[a]

pressure MPa	$\Delta H^\ddagger$kJ mol^{-1}	$\Delta S^\ddagger$ J mol^{-1} K^{-1}	$\Delta G^\ddagger$ (303 K) kJ mol^{-1}
(a) reaction conditions: **3a** (5 mM) in $CDCl_3$/DMSO-d_6 (1:1)			
0.1	46 ± 0.5	−187 ± 1.7	102.4 ± 0.6
100	64 ± 2.2	−124 ± 7.1	101.1 ± 0.2
200	75 ± 0.9	−86 ± 2.9	100.7 ± 0.4
300	83 ± 2.5	−58 ± 7.8	100.3 ± 0.4
(b) reaction conditions: **3b** (2 mM) in $CDCl_3$/DMSO-d_6 (2:1)			
0.1	80 ± 2.7	−73 ± 8.6	102.2 ± 0.1
100	93 ± 2.5	−30 ± 7.8	101.6 ± 0.1
200	101 ± 1.9	1 ± 6.0	101.8 ± 0.1
300	117 ± 2.5	52 ± 8.0	101.7 ± 0.1

[a] These parameters were determined from the Eyring plots in Figure 4.

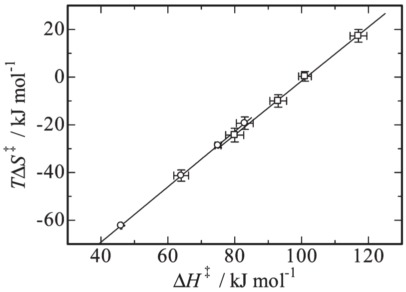

FIGURE 5. Enthalpy/entropy compensation plots for the decomplexation of the [2]pseudorotaxanes **3a** (○) and **3b** (□).

Conclusion

We have studied the formation and dissociation of [2]pseudorotaxanes comprising crown ethers and secondary ammonium ions in aprotic nonpolar solvents at high pressure. Complexation was enhanced under high pressure; the relationships between the rate constant and the pressure revealed negative activation volumes. Decomplexation of the [2]pseudorotaxanes in polar solvents was also enhanced under high pressure. Kinetic studies of variable-temperature and -pressure data provided us with the kinetic parameters for the decomplexation processes, revealing that they also occurred with negative activation volumes.

Figure 6 displays the volume profiles for the formation and decomplexation of the [2]pseudorotaxanes. The formation process is characterized by a substantial decrease in volume upon proceeding from the free species to the transition states, followed by an increase in volume upon reaching the complexes. Because the solvent systems that we employed for the formation and decomplexation processes were different, the degree of solvation of the transition states cannot be compared directly. Nevertheless, one possibility for the negative volumes for both the complexation and decomplexation processes can be attributed to the complementary sizes of the terminal units of the dumbbell-like axles and the cavities of the crown ethers; another is that solvation might contribute to the negative activation volumes.

Experimental Section

Kinetic Measurement of the Formation of the [2]Pseudorotaxanes (3). Solutions of 30 mM **1a** in $CDCl_3$ and 30 mM **2a** in CD_3CN were prepared separately. Mixtures of the two solutions (2 mL each) were pressed at various pressures and

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[31] We also estimated the kinetic data for the formation of the [2]pseudorotaxanes, but the correlation between the activation enthalpy and the activation entropy was poor, presumably because we neglected to consider the changes in the association constants for ion pairing between the ammonium and hexafluorophosphate ions at elevated temperatures and pressures. Nevertheless, the tendency of the parameters upon increasing pressure were similar to those for [2]pseudorotaxane decomplexation: (1) the activation free energies ($\Delta G^\ddagger$) for [2]pseudorotaxane formation were similar at all pressures; (2) the activation enthalpy ($\Delta H^\ddagger$ and entropy ($\Delta S^\ddagger$) increased upon increasing pressure; (3) the activation enthalpy and entropy of **3a** were both smaller than those of **3b**. See the Supporting Information for additional details.

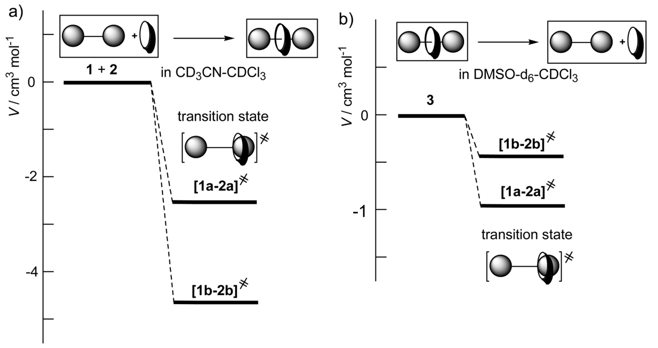

FIGURE 6. Volume profile for the formation (a) and decomplexation (b) of the [2]pseudorotaxanes at 298 K and zero pressure.

temperatures. For each pressure and temperature, more than four samples were taken and analyzed (^{1}H NMR spectroscopy) after dilution of the sample twice with CDCl$_3$/CD$_3$CN (1:1). The concentrations of **2a** were calculated through integrations of benzylic protons of **2a** and **3a** in the ^{1}H NMR spectra. In a similar manner, 10 mM solutions of **1b** and **2b** in CDCl$_3$/CD$_3$CN (2:1) were prepared and the rate constants measured by monitoring ^{1}H NMR spectra at appropriate times (duplicated at least four times).

Kinetic Measurement of the Decomplexation of the [2]-Pseudorotaxanes (3). Solutions of **3a** (5 mM) and **3b** (2 mM) in CDCl$_3$/DMSO-d_6 (1:1 for **3a**; 2:1 for **3b**) were prepared separately and then samples (2 mL) were pressed at various pressures and temperatures. For each pressure and temperature, more than four samples were taken and analyzed with ^{1}H NMR spectroscopy.

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Supporting Information Available: kinetic data for the complexation of **1a** and **2a** at various pressures, kinetic data for the complexation of **1b** and **2b** at various pressures, kinetic data for the dissociation of the [2]pseudorotaxane **3a** at various temperatures, kinetic data for the dissociation of the [2]pseudorotaxane **3b** at various temperatures, *k* values for the dissociation of pseudorotaxanes **3a** and **3b**, Eyring plots for the formation of the [2]pseudorotaxanes **3a** and **3b**, kinetic parameters for the complexation of the [2]pseudorotaxanes **3a** and **3b** under various pressures, and NMR spectra of compounds **1b**, **2a**, and **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.