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Variable-Temperature and Variable-Pressure Sodium-23 NMR Study on Dissociation Reaction of Sodium(I) Cryptates in Ethylenediamine

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The dissociation rates of the sodium(I) cryptates of 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane (C221) and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (C222) in ethylenediamine have been measured at various temperatures and pressures by the ^{23}Na NMR line-broadening method. The dissociation rate constant at 298 K (k_d^{298}), activation enthalpy ($\Delta H^\ddagger$), activation entropy ($\Delta S^\ddagger$), and activation volume ($\Delta V^\ddagger$) are as follows: $k_d^{298}=7.2\ \mathrm{s}^{-1}$, $\Delta H^\ddagger=45.9\pm1.8\ \mathrm{kJ\,mol}^{-1}$, and $\Delta S^\ddagger=-74.5\pm5.4\ \mathrm{J\,mol}^{-1}\,\mathrm{K}^{-1}$ for Na$^+$C221, and $k_d^{298}=272\ \mathrm{s}^{-1}$, $\Delta H^\ddagger=43.2\pm1.1\ \mathrm{kJ\,mol}^{-1}$, $\Delta S^\ddagger=-53.6\pm3.7\ \mathrm{J\,mol}^{-1}\,\mathrm{K}^{-1}$, and $\Delta V^\ddagger=8.9\pm0.4\ \mathrm{cm}^3\,\mathrm{mol}^{-1}$ for Na$^+$C222. The large positive value of $\Delta V^\ddagger$ for Na$^+$C222 indicates the dissociative transition state accompanied by the expansion of the cavity of C222. The electrostatic interaction of the sodium cation with ethylenediamine in the transition state has been discussed in connection with the other solvents by comparison of the values of $\Delta H^\ddagger$.

It is important to clarify the behavior of alkali metal cations in various solvents in order to understand the properties of the solvents and the reactivities of the alkali metal ions. However, it is difficult to directly observe the interaction between the alkali metal cation and the solvent molecule. In contrast, the structural and kinetic properties of the alkali metal cryptates in a variety of solvents have been extensively investigated.[1—31] Some of these studies have revealed that the dissociation rates of alkali metal cryptates are quite sensitive to the properties of the solvents.[2,14,18,24,26,28,30] Such an effect of solvents can be attributed to the interaction of the solvents with the alkali metal cations of the cryptates in the transition state. Accordingly, the interaction will be elucidated by observing the dissociation reaction of the alkali metal cryptates as a probe. From this point of view, the comparison of the activation parameters for the dissociation reactions in various solvents is required.

While the dissociation reactions of various kinds of alkali metal cryptates have so far been studied by the NMR line-broadening method,[1,2,5,8,18,24,26,28,30] there have only been a few reports of activation parameters for sodium(I) cryptate of 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane (Na$^+$C221) which were obtained by using a stopped-flow apparatus.[27] This is because the dissociation rates are too slow for measurement by the NMR method due to the high stability of Na$^+$C221. On the other hand, it has been claimed that the dissociation rates of alkali metal cryptates increase in the stronger donating solvents.[2,14,18,24,26,28,30] Therefore, it may be possible to measure the dissociation rate for Na$^+$C221 by the NMR method using ethylenediamine (EN) as a solvent which has a strong donicity with an anomalously large donor number (DN=55).[32] Furthermore, it is of great interest to see to what extent the interaction between the sodium(I) ion and EN as a solvent is actually operating, as this is scarcely known, although EN is common as a ligand for the transition metal ions.

In the present work, we have measured the dissociation rates for Na$^+$C221 and sodium(I) cryptate of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Na$^+$C222) in EN by the NMR method and have compared the activation parameters. Furthermore, $\Delta V^\ddagger$ for the dissociation reaction of Na$^+$C222 has been determined by using a high-pressure NMR apparatus.[33] This appears to be the first instance of the determination of $\Delta V^\ddagger$ for dissociation of cryptate by the variable-pressure NMR method, and not by a stopped-flow technique.[27,34] The kinetic parameters in EN have been compared with those for Na$^+$C221 in *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) previously obtained[27] in order to reveal the difference in interaction between the sodium(I) ion and the solvent molecules. We will also discuss the application of $\Delta H^\ddagger$ to characterization of the solvents.

Experimental

Ethylenediamine (EN) was purified by the same procedure as previously described.[35] Sodium nitrate was recrystallized from distilled water twice and dried at ca. 330 K. Cryptand ligands, C211 (4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane), C221, and C222 were purchased from Merck Co. and used without further purification. The sample preparations for NMR measurements were carried out in a glove box by using freshly distilled EN. The sample solutions for variable-temperature NMR measurements were sealed under vacuum in 5-mm o.d. NMR tubes that were coaxially mounted in 10-mm o.d. NMR tubes containing D_2O as a lock solvent. For variable-pressure NMR measurements, a 7-mm o.d. NMR tube capped with a flexible teflon tube was used.[33]

^{13}C and ^{23}Na NMR measurements were performed on a JEOL JNM-GX 270 FT-NMR spectrometer operating at 67.89 and 71.32 MHz, respectively. In variable-temperature NMR measurements, the temperature of the sample solutions was measured by a substitution technique using a thermistor (D641, Takara Thermistor Co.). About 15 min were required for the temperature equilibration and the temperature stability was ± 0.1 K. The variable-pressure NMR measurements were carried out by using a high-pressure NMR probe constructed for the wide-bore superconducting magnet (6.34 T) of a JEOL JNM-GX 270 FT-NMR spectrometer.[33] The pressure generated by a pressure-generating pump (KBP56, Hikarikouatu Co., Hiroshima) was measured with a Heise Bourdon gauge. Daifloil (No. 1, poly(chlorotrifluoroethylene), Daikin-kogyo Co.) was used as a pressure-transmitting liquid. The temperature of the sample solution was measured by a substitution technique with a thermistor and monitored with a thermocouple introduced into a pressure vessel during the high pressure experiments. About 5—8 h were required for the complete temperature equilibration and the temperature stability was ± 0.2 K.

Results and Discussion

Cryptate complexes of the alkali metal ions exist either in the 'inclusive' form, in which the metal ion resides in the center of the approximately spherical cavity of cryptand, or in the 'exclusive' form, in which the metal ion resides outside the cryptand cavity.[5,17,18,25,36—38] X-Ray structural studies indicate that Na^+C211 exists in the exclusive form and Na^+C221 and Na^+C222 in the inclusive form.[25,36—38] The NC–CO torsion angles in the inclusive form of the sodium(I) cryptate decrease from those in the free cryptand due to the electrostatic interaction between the sodium(I) ion and the donor atoms of cryptand, although such a distinctly conformational change is not observed in the exclusive form.[17,18] Steric crowding of proton-bearing carbon atoms due to the decrease in the torsion angles results in their being shielded and the upfield shift of ^{13}C NMR signals. Therefore, the structure in solution can be confirmed by the ^{13}C NMR chemical shift.[17,39]

Figure 1 shows the ^{13}C NMR spectra of the cryptands and sodium(I) cryptates in EN solution for the three cryptands. The assignment of each carbon atom is made by comparison with that in deuterated chloroform solution in the literature[17,18] and by consideration of the relative peak intensity. The shifts of all the resonance lines for Na^+C221 and Na^+C222 are upfield from the corresponding resonance lines of the free cryptands, whereas Na^+C211 exhibits no substantial upfield shift. These facts indicate that Na^+C221 and Na^+C222 exist in the inclusive form and Na^+C211 in the exclusive form in EN solution. As apparent from Fig. 1, the resonance lines corresponding to the free cryptand are not observed in the ^{13}C NMR spectrum for each solution of the sodium(I) cryptates under the present conditions where the total concentration of the sodium(I) ion is about twice as much as that of the cryptand. Furthermore, the observed resonance lines are not coalesced because these resonances did not shift even by change in the mole ratio of the cryptand to the sodium(I) ion. These findings indicate that the sodium(I) cryptates are formed quantitatively in EN under these conditions.

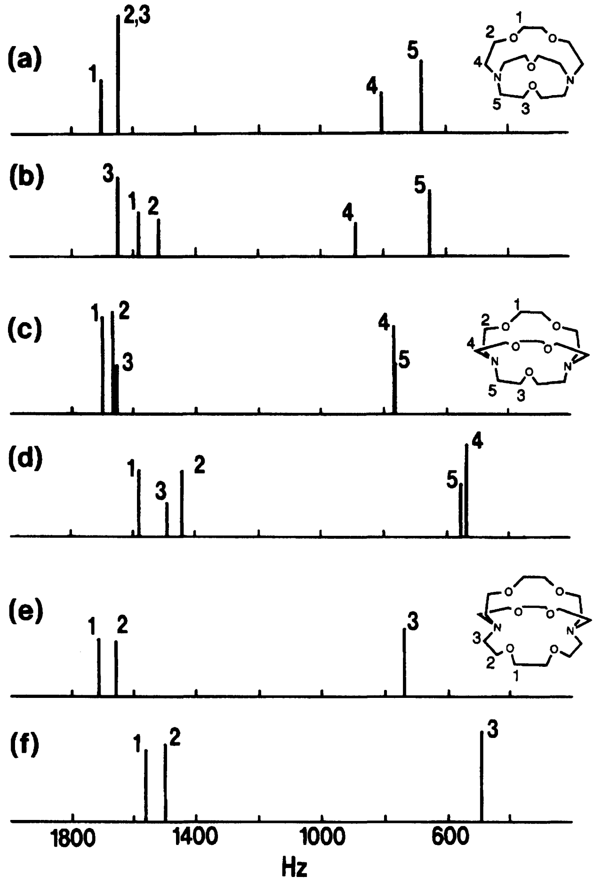

Fig. 1. ^{13}C NMR spectra of the free cryptands and sodium(I) cryptates in EN solution. (a) C211 (8.88×10^{-2} mol kg^{-1}); (b) the mixture of C211 (4.60×10^{-2} mol kg^{-1}) and $NaNO_3$ (9.30×10^{-2} mol kg^{-1}); (c) C221 (1.69×10^{-1} mol kg^{-1}); (d) the mixture of C221 (1.35×10^{-1} mol kg^{-1}) and $NaNO_3$ (2.76×10^{-1} mol kg^{-1}); (e) C222 (1.80×10^{-1} mol kg^{-1}); (d) the mixture of C222 (1.50×10^{-1} mol kg^{-1}) and $NaNO_3$ (3.34×10^{-1} mol kg^{-1}). Chemical shifts are given versus methylene carbon of EN.

As shown in Fig. 2, the ^{23}Na NMR spectra for Na^+C221 and Na^+C222 in EN solution containing a comparable amount of free sodium(I) ion showed the two-site exchange of the sodium(I) ion between the cryptate and solvated state (Fig. 2(b) and (c)). On the other hand, only one ^{23}Na NMR signal was observed for the solution of Na^+C211 with a similar chemical shift to that of the solvated sodium(I) ion (Fig. 2(a)). This suggests a similar magnetic environment of the sodium(I) ion in Na^+C211 with the exclusive form and in the solvated state, resulting in the close chemical shifts to each other and, consequently, the coalesced signal.

The rate constant (k_{ex}) for the sodium ion exchange between the cryptate and solvated state in the case of Na^+C221 and Na^+C222 are given by Eq. 1:

$$k_{ex} = \tau_c^{-1} = \tau_s^{-1}[S]/[C] = \pi(\Delta\nu_{obsd} - \Delta\nu_{solv})[S]/[C], \quad (1)$$

where τ_c and τ_s are the mean life times of sodium(I)

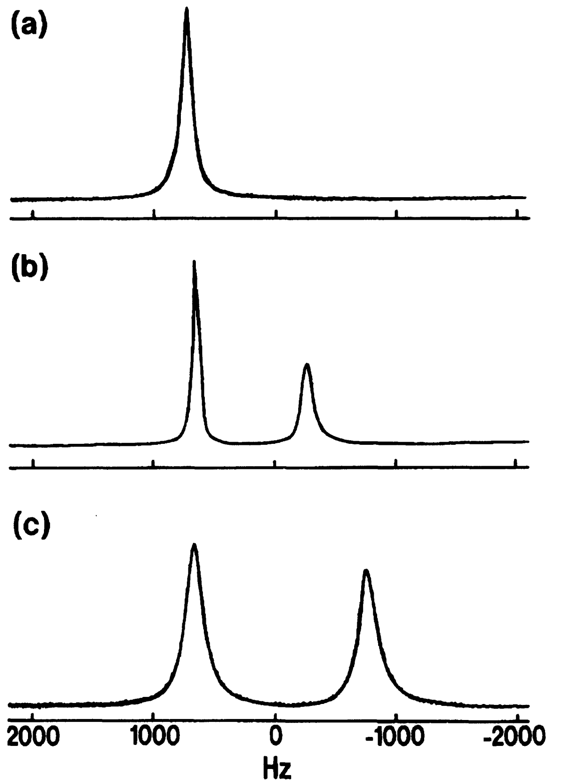

Fig. 2. ^{23}Na NMR spectra of EN solutions of the sodium(I) cryptate and free sodium(I) ion at 303 K. (a) Na^+C211 (4.85×10^{-1} mol kg^{-2}), Na^+ (4.99×10^{-2} mol kg^{-1}); (b) Na^+C221 (2.18×10^{-1} mol kg^{-1}), Na^+ (2.27×10^{-1} mol kg^{-1}); (c) Na^+C222 (2.18×10^{-1} mol kg^{-1}), Na^+ (2.27×10^{-1} mol kg^{-1}). The resonances of Na^+C221 and Na^+C222 appear upfield from that of the solvated Na^+. Chemical shifts are given versus Na^+ in a lock solvent (D_2O).

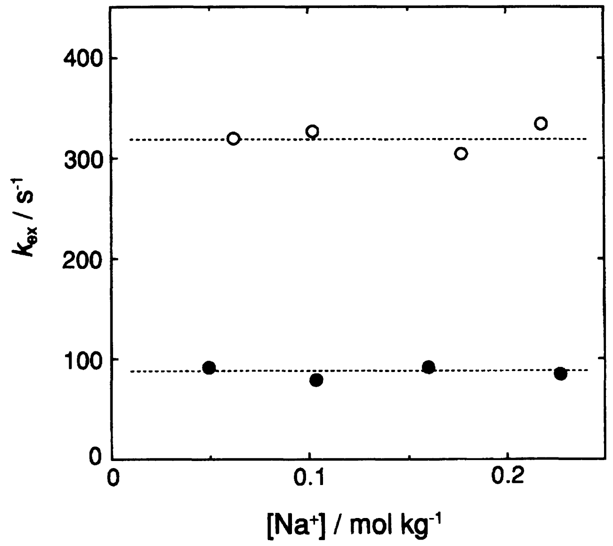

Fig. 3. Dependence of exchange rate constants on the concentration of the free sodium(I) ion. ●: Na^+C221 at 340.6 K ($[Na^+C221]=5.8\times10^{-2}$ mol kg^{-1}); ○: Na^+C222 at 302.6 K ($[Na^+C222]=4.8\times10^{-2}$ mol kg^{-1}). Sodium nitrate was used to vary $[Na^+]$.

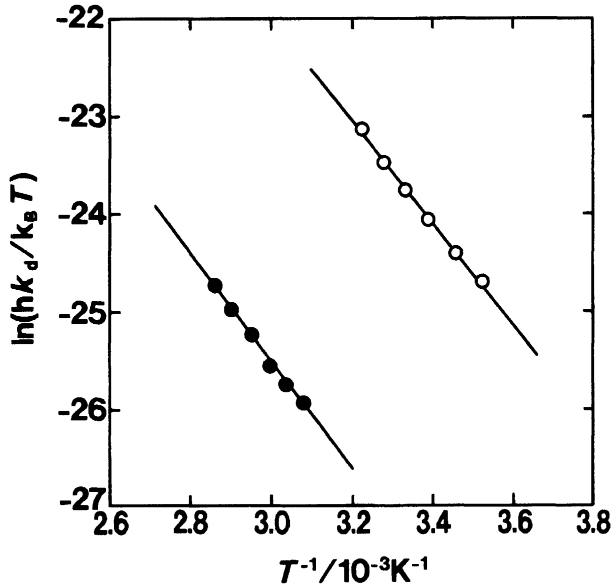

Fig. 4. Temperature dependence of dissociation rate constants for Na^+C221 (●) and Na^+C222 (○) at atmospheric pressure. k_B is the Boltzmann constant and h is the Plank constant.

cryptate and the solvated sodium(I) ion, respectively, [C] and [S] are the concentrations of the corresponding species, and $\Delta\nu_{obsd}$ and $\Delta\nu_{solv}$ are the half-height widths of the NMR signals of the solvated sodium(I) ion, respectively, in the presence and absence of the cryptand ligands. The rate constants were calculated by using observed half-height widths. It is seen from Fig. 3 that k_{ex} for each cryptate is independent of the concentration of the solvated sodium(I) ion within experimental errors. This finding indicates that the monomolecular mechanism for the dissociation of the sodium(I) ion from the cryptate followed by a quite rapid formation of the cryptate is operative in the sodium ion exchange process. This is consistent with no observation of the free cryptands from the ^{13}C NMR spectra as described above. Consequently, k_{ex} corresponds to the dissociation rate constant, k_d.

The variable-temperature results of k_d for Na^+C221 and Na^+C222 were fitted to the Eyring equation $\ln(hk/k_BT)=-\Delta H^\ddagger/RT+\Delta S^\ddagger/R$ as shown in Fig. 4. The pressure dependence of k_d for Na^+C222 shows the linear plot of $\log k_d$ versus pressure, P (Fig. 5). The volume of activation is given by $\Delta V^\ddagger=-RT(\partial\ln k_d/\partial P)_T$. In the case of Na^+C221, not enough broadening of the ^{23}Na NMR resonance line of the solvated sodium(I) ion compared to the reference line width was observed because the half-height width of the reference line by using the high-pressure NMR probe is too wide (ca. 0.8 ppm) mainly due to nonspinning and inhomogeneous environment.[33] The rate constants and activation parameters for the dissociation reactions of the sodium(I)

Table 1. Rate Constants and Activation Parameters for Dissociation Reactions for Sodium(I) Cryptates

Cryptand	Solvent	k_d^{298}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta V^{\ddagger}$	Ref.
		s^{-1}	$kJ\,mol^{-1}$	$J\,mol^{-1}\,K^{-1}$	$cm^3\,mol^{-1}$	
C221	EN	7.2	45.9±1.8	−74.5±5.4		This work
C222	EN	272	43.2±1.1	−53.6±3.7	8.9±0.4	This work
		3×10^2				a)
C221	DMF	0.337	73.0±0.9	− 9 ±3	2.0±0.2	b)
C221	DMSO	0.765	70.4±0.8	−11 ±3	2.1±0.7	b)

a) Ref. 8 (at 303 K). b) Ref. 27.

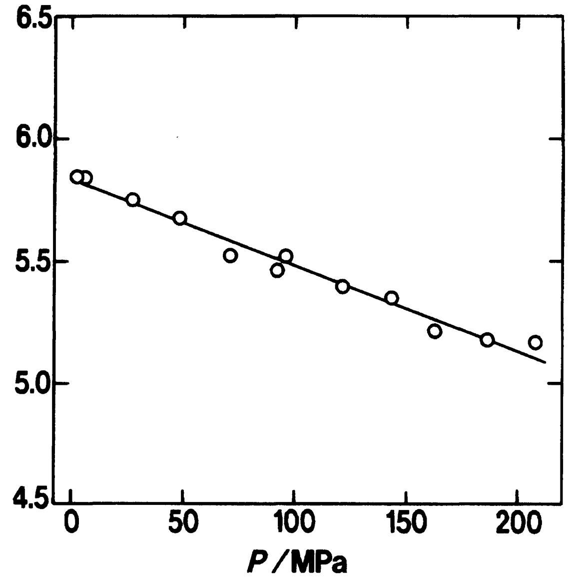

Fig. 5. Pressure dependence of dissociation rate constants for Na^+C222 at 303.7 K.

ion in EN are summarized in Table 1 together with those in DMF and DMSO previously obtained.[27)]

It has been proposed that the transition state of the dissociation reactions for Na^+C221 and Na^+C222 takes a structure analogous to the exclusive form.[18)] If the electrostriction due to the partial exposure of the sodium(I) ion to the solvent in the transition state is the major factor for the volume change, a negative value of $\Delta V^{\ddagger}$ should be observed. In fact, however, the values of $\Delta V^{\ddagger}$ in Table 1 are positive. Therefore, the increase in volume due to projection of the sodium(I) ion into the solvent mainly contributes to the volume change, and the charge localization in the transition state is a minor factor and/or the electrostriction of the partially solvated sodium(I) ion in the transition state is cancelled out by the desolvation of the neutral cryptand ligand.

Interestingly, the dissociation reaction for Na^+C222 in EN shows a considerably large value of $\Delta V^{\ddagger}$ compared to those for Na^+C221 in DMF and DMSO. The difference in $\Delta V^{\ddagger}$ may come from the difference in degree of dissociation of the sodium ion in the transition state between Na^+C222 and Na^+C221, that is, the dissociation for Na^+C222 is much more promoted than that for Na^+C221. Taking into account the fact that the cavity size of Na^+C221 is similar to that of free C221,[36,41)] we can assume that the cavity size does not change in the transition state. Consequently, the activation volume simply corresponds to the volume of the sodium(I) ion which partially emerges out of the cryptand cavity. By calculating from the ion radius of the sodium(I) ion, 1.16 Å,[40)] which gives 3.9 $cm^3\,mol^{-1}$ to the volume of the sodium(I) ion, it is expected from the $\Delta V^{\ddagger}$ values for Na^+C221 in DMF and DMSO that about half the sodium(I) ion is out of the cryptand cavity in the transition state. In contrast, the much larger $\Delta V^{\ddagger}$ value of 8.9 $cm^3\,mol^{-1}$ for Na^+C222 is not attributable only to the volume of the sodium(I) ion emerging out of C222. In the solid state, the cavity size for Na^+C222 is compressed in comparison with that for the free C222 ligand.[37,41,42)] The internal radius of the cavity of Na^+C222 has been estimated to be by ca. 0.2 Å shorter than that for free C222 (ca. 1.4 Å) which is close to that of K^+C222.[41)] This implies that the difference in the volume of the cavity between free C222 and Na^+C222 is ca. 2.6 $cm^3\,mol^{-1}$, and accordingly the difference in the external volumes is much larger. By considering such an electrostatic interaction between the donor atoms of C222 and the central cation, the expansion of the cavity should be observed in the transition state for the dissociation reaction of Na^+C222 and results in the much larger $\Delta V^{\ddagger}$ value than that of Na^+C221. The difference in structure of the transition state between Na^+C221 and Na^+C222 is consistent with the fact that the $\Delta S^{\ddagger}$ for Na^+C222 shows a less negative value than that for Na^+C221 in the same solvent, EN (Table 1). The difference in $\Delta S^{\ddagger}$ causes the considerable difference in k_d between Na^+C222 and Na^+C221 in EN.

As shown in Table 1, the dissociation rate (k_d) for Na^+C221 in EN is increased about one order of magnitude over those in DMF and DMSO. The large k_d value in EN can be ascribed to the small value of $\Delta H^{\ddagger}$ because $\Delta S^{\ddagger}$ in EN is much more negative than those in DMF and DMSO. The smaller $\Delta H^{\ddagger}$ value in EN indicates the large solvation energy obtained in the transition state with the partially solvated sodium(I) ion. Thus it is clear that the electrostatic interaction of the sodium(I) ion with EN is much stronger than those with DMF and

DMSO.

It has been claimed that the dissociation rates of the cryptates are correlated with Gutmann's donor numbers of solvents.[14,24,26,28,30] However, this does not seem to be a reasonable approach, for the reasons described below. The entropic term contained in the activation energy may not be reflected by Gutmann's donor number, which is simply the heat of complexation between the solvent molecule and antimony pentachloride. Therefore, $\Delta H^{\ddagger}$ instead of k_d should be correlated with the donor number. Furthermore, the donor number itself has some problems as an empirical parameter. For example, the comparison of the donor number is achieved on the assumption that the enthalpy change in the structural change for adduct formation from a bipyramidal (sp^3d hybridization) to the distorted octahedral configuration is negligible. The more serious problem of applying the donor number to the discussion about the solvation of the alkali metal ion is the difference in the bonding character between the antimony and the alkali metal ion toward the solvent molecule. The bonding energy of the solvent adduct of $SbCl_5$ is affected by the relative energy level of the atomic orbitals of the antimony and the donor atom of the solvent molecule. On the other hand, the bonding between the alkali metal cation and the donor atom of the solvent is formed by an electrostatic interaction. Thus, the values of $\Delta H^{\ddagger}$ for the dissociation reactions of alkali metal cryptates more accurately reflect the strength of the electrostatic interaction between the alkali metal ion and the donor atoms of the solvents.

The above discussion suggests that the values of $\Delta H^{\ddagger}$ for dissociation of alkali metal cryptates are applicable to the estimation of the solvating ability of the solvents toward alkali metal cations. Though there have been some systematic studies to estimate the solvating ability by using the ^{23}Na NMR chemical shifts of the solvated sodium(I) ion,[43,44] in some cases, the chemical shifts depend on the concentration of the sodium salt, which may be due to the ion pairing effect. However, such a concentration dependence is not observed in the dissociation reaction in the present work. Moreover, we can control the dissociation rate to be measurable by using the same size cryptand with a different number of the donor atoms. For example, we can use 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.5]tricosane ($C22C_5$)[31] instead of C221 to accelerate the dissociation rate because the electrostatic interaction between the sodium(I) ion and the donor atoms of $C22C_5$ is expected to be smaller than that of C221, as reported in the case of 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane ($C21C_5$) in comparison with C211.[30]

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