

# Exchange Kinetics of the Sodium Cation with Dibenzo-24-crown-8 in Nitromethane Solution: Competition between Unimolecular Decomplexation and Bimolecular Cation Interchange Mechanisms

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**Abstract:** Exchange kinetics for the complexation-decomplexation reaction of sodium tetraphenylborate with the ligand dibenzo-24-crown-8 in nitromethane have been studied by Na-23 nuclear magnetic resonance. At low concentrations of sodium tetraphenylborate and crown ( $<10^{-3}$  M, 295 K), two different resonances are observed for complexed and solvated sodium cations and the measured rate constants for the sodium-exchange process are independent of the total sodium concentration: the mechanism is a unimolecular decomplexation. A concentration coalescence is observed for  $[\text{NaBPh}_4]$  and  $[\text{crown}] = 5 \times 10^{-3}$  M (295 K). At higher concentrations, the combined data of transverse and longitudinal relaxation rates show that the complexation/decomplexation process obeys a bimolecular cation interchange mechanism whose kinetic parameters are  $\Delta H^\ddagger = 31 \pm 3$  kJ mol<sup>-1</sup> and  $\Delta S^\ddagger = -32 \pm 10$  J K<sup>-1</sup> mol<sup>-1</sup>. An estimation can be given for the energy barrier of the unimolecular decomplexation process:  $\Delta G^\ddagger_{\text{uni}} \approx 65$  kJ mol<sup>-1</sup> (300 K).

Efficient natural ionophores are characterized by ion complexation-decomplexation reactions proceeding at a sufficiently rapid rate, which reflects a compromise between ion affinity and ion-exchange kinetics.<sup>1</sup> If synthetic ligands such as cryptands<sup>2</sup> or spherands<sup>3</sup> display high affinity and selectivity for alkali-metal cations, they very slowly release the encaged cation. Large crown ethers<sup>4</sup> are conformationally versatile and can adopt a stable conformation which allows them to wrap around the alkali-metal cation. This is the case with the dibenzo-30-crown-10 (DB30C10) complex with K<sup>+</sup> in the solid state<sup>5</sup> or in solution,<sup>6</sup> or with the dibenzo-24-crown-8 (DB24C8) complex with Na<sup>+</sup> in solution.<sup>7</sup> In the latter case, solvent molecules and the counteranion are expelled from the first coordination sphere of Na<sup>+</sup> after complexation has occurred,<sup>7</sup> giving a structure similar to the cryptand case where the cation is isolated from the environment. In the case of large crown ethers, we are thus in the presence of a three-dimensional cationic recognition, which is analogous to the two-dimensional recognition displayed by smaller crowns. This three-dimensional conformation-based recognition should give complexes much more labile than complexes resulting from the constitution-based recognition occurring with cryptands.

Alkali-metal cation NMR is an efficient tool for the study of such kinetics<sup>8</sup> and has been applied to a few cases of smaller crowns,<sup>9-12</sup> cryptands,<sup>13,14</sup> or natural ionophores.<sup>15</sup>

Lin and Popov<sup>16</sup> have shown that the exchange between solvated and 18C6-complexed sodium is slow on the NMR time scale at 25 °C in tetrahydrofuran, when the counteranion is tetraphenylborate but not perchlorate or iodide. Analyzing potassium-39 NMR line shapes, Schmidt and Popov<sup>17</sup> studied the kinetics of complexation of potassium cation with the crown ether 18-crown-6 in five solvents or solvent mixtures. They found that the cation exchange proceeds via a unimolecular process in 1,3-dioxolane. This finding is somewhat unique, the only other reported example being the system F1-Na<sup>+</sup>/dimethyl-DB18C6 in the THF-d<sub>3</sub>.<sup>18</sup> Chock has made a study of the complexation-decomplexation reactions of Na<sup>+</sup> by DB30C10 in methanol by temperature-jump relaxation, showing evidence for a conformational change before the actual complexation step (19).

We show in this paper that two mechanisms are operative for the decomplexation of sodium complexed by DB24C8 in nitromethane: an efficient bimolecular cation interchange mechanism in which the rate-controlling step necessitates the approach of two sodium cations on the same ligand and, at low concentrations of

sodium tetraphenylborate and crown ether, the classical unimolecular decomplexation mechanism which has been shown to be the actual mechanism of decomplexation for smaller crowns.<sup>9,10</sup> The bimolecular mechanism is characterized by the activation parameters  $\Delta H^\ddagger = 31$  kJ mol<sup>-1</sup> and  $\Delta S^\ddagger = -32$  J K<sup>-1</sup> mol<sup>-1</sup>.

## Results

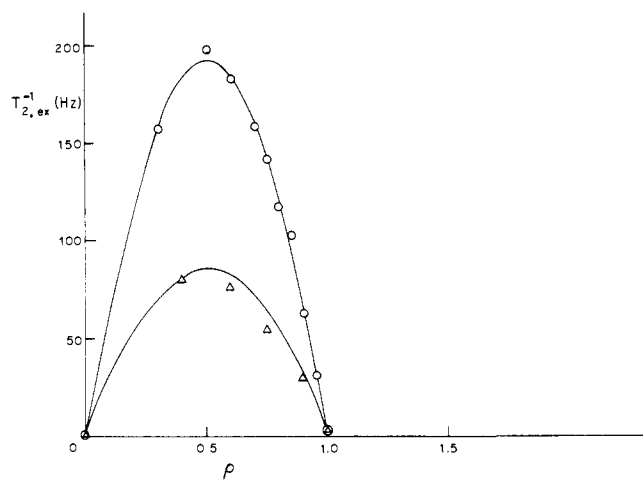
In the preceding paper<sup>20</sup> in this issue, we have shown that a model based on sodium-crown aggregation accounts for the experimentally observed longitudinal relaxation rate data. The variations of  $\ln T_2^{-1}$  and  $\ln T_1^{-1}$  with  $\ln T^{-1}$  are linear with different slopes (Figure 4 of the preceding paper<sup>20</sup>) which shows that the observed transverse relaxation rate,  $T_2^{-1}$ , is affected by chemical exchange ( $T_{2,\text{ex}}^{-1}$ ) in addition to inhomogeneities ( $T_{2,\text{inh}}^{-1}$ ) and quadrupolar contributions ( $T_{2,\text{q}}^{-1}$ ) (eq 1).

$$T_{2,\text{obsd}}^{-1} = T_{2,\text{inh}}^{-1} + T_{2,\text{ex}}^{-1} + T_{2,\text{q}}^{-1} \quad (1)$$

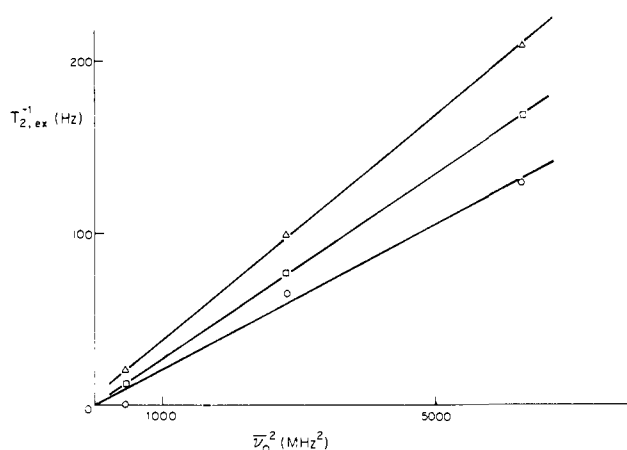
In the extreme narrowing limits,  $T_{1,\text{obsd}}^{-1} \equiv T_{1,\text{q}}^{-1} \equiv T_{2,\text{q}}^{-1}$ .  $T_{2,\text{inh}}^{-1}$

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**Figure 1.** Chemical-exchange contribution to the Na-23 transverse relaxation rate for sodium tetraphenylborate (concentration: 0.037 M) in the presence of dibenzo-24-crown-8 in nitromethane as a function of  $\rho$  = [DB24C8]/[Na<sup>+</sup>]. (O) 79.35 MHz; ( $\Delta$ ) 52.92 MHz.



**Figure 2.** Chemical-exchange contribution to the Na-23 transverse relaxation rate for NaBPh<sub>4</sub> (0.037 M) in the presence of DB24C8 ([DB24C8]/[Na<sup>+</sup>] = 0.50 ( $\Delta$ ), 0.80 (O), and 0.30 ( $\square$ )) as a function of  $\bar{\nu}_o^2$ , the square of the observation frequency.

is given by  $T_{2,obsd}^{-1} - T_{1,obsd}^{-1}$  in the cases of  $\rho = 0$  and  $\rho > 1.0$  ( $\rho = [\text{crown}]/[\text{sodium}]$ ), where the exchange contribution is negligible and is equal to  $11 \pm 3$  Hz, at 295 K.

A plot of  $T_{2,ex}^{-1} (=T_{2,obsd}^{-1} - T_{1,obsd}^{-1} - T_{2,inh}^{-1})$  against  $\rho$  is given on Figure 1 at 79.35 and 52.92 MHz. After subtraction of the quadrupolar contributions, the two curves match well in phase (see Figure 2, preceding paper in this issue for the graph of  $T_{2,obsd}^{-1}$  against  $\rho$ ). They display a maximum for a ratio  $\rho = 0.50$ . It is gratifying to note that  $(T_{2,ex}^{-1})_{79.35}/(T_{2,ex}^{-1})_{52.92} = 2.2 \pm 0.1$  while the ratio of the square of the observation frequencies is equal to 2.25. At 21.04 MHz,  $T_{2,ex}^{-1}$  remains below 20 Hz in the full range of  $\rho$  values. Figure 2 shows the dependence of  $T_{2,ex}^{-1}$  with the square of the frequency of observation for the three ratios  $\rho$ . The relationships are linear and a slope with a maximum value is observed for  $\rho = 0.50$ . All those observations are in agreement with a moderately rapid-exchange model where  $T_{2,ex}^{-1}$  is given by eq 2 for a two-site case<sup>21</sup> where  $P_A$  and  $P_B$  are the populations

$$T_{2,ex}^{-1} = 4P_AP_B\pi^2(\nu_A - \nu_B)^2(k_A + k_B)^{-1} \quad (2)$$

of sites A and B,  $\nu_A$  and  $\nu_B$  their chemical shift expressed in hertz, and  $k_A$  and  $k_B$  the inverse of the sodium lifetime in sites A and B, respectively.

In the preceding paper in this issue, we have shown the existence in solution of aggregated  $(n + 1)/n$  sodium/crown species.<sup>20</sup> The fact that their population is very small ( $\leq 2\%$ ) and that the dif-

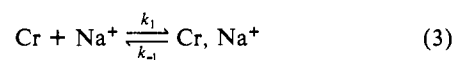
**Table I.**

$\rho^a$	$T_{1,obsd}^{-1},^b$ Hz	$T_{2,obsd}^{-1},^c$ Hz	$T_{2,ex}^{-1},^d$ Hz	$k_A + k_B,^e$ $10^4$ Hz
0	22 $\pm$ 1	30 $\pm$ 3		
0.30	110 $\pm$ 3	278 $\pm$ 6	157 $\pm$ 9	1.3 $\pm$ 0.1
0.50	162 $\pm$ 4	370 $\pm$ 7	197 $\pm$ 11	1.3 $\pm$ 0.1
0.60	191 $\pm$ 5	385 $\pm$ 7	183 $\pm$ 12	1.3 $\pm$ 0.1
0.70	217 $\pm$ 10	386 $\pm$ 7	158 $\pm$ 17	1.3 $\pm$ 0.1
0.75	225 $\pm$ 3	377 $\pm$ 7	141 $\pm$ 10	1.3 $\pm$ 0.1
0.80	236 $\pm$ 6	365 $\pm$ 7	118 $\pm$ 13	1.3 $\pm$ 0.1
0.85	243 $\pm$ 5	356 $\pm$ 7	103 $\pm$ 12	1.2 $\pm$ 0.1
0.90	253 $\pm$ 7	327 $\pm$ 6	63 $\pm$ 13	1.4 $\pm$ 0.3
0.95	253 $\pm$ 5	296 $\pm$ 6	32 $\pm$ 11	1.5 $\pm$ 0.5
1.00	208 $\pm$ 5	222 $\pm$ 5		
1.15	205 $\pm$ 4	218 $\pm$ 5		

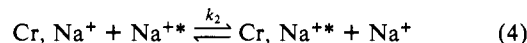
<sup>a</sup> Ratio of [crown] over [NaBPh<sub>4</sub>] for a constant sodium concentration (=0.037 M) ( $\Delta\nu = \nu_A - \nu_B = 499$  Hz, see eq 2). <sup>b</sup> Observed longitudinal relaxation rate; the reported error is taken as equal to  $3\sigma$ ,  $\sigma$  being the standard deviation obtained from the nonlinear regression analysis. <sup>c</sup> Observed transverse relaxation rate. <sup>d</sup> Exchange contribution to the relaxation rate,  $T_{2,ex}^{-1} (=T_{2,obsd}^{-1} - T_{2,inh}^{-1} - T_{1,obsd}^{-1})$ . <sup>e</sup> Sum of the pseudo-first-order rate constants for the two-sites exchange process ( $(k_A + k_B) = (13 \pm 1) \times 10^3$  Hz) at 295 K.

ference of the chemical shifts between aggregated species and 1:1 complexed sodium is expected to be small allows us to neglect the contribution of the aggregates to the exchange broadening and to treat the problem as a pure two-site system. However, this will be true only if the exchange barrier connecting the aggregated species and the 1:1 complex is of the same order of magnitude or lower than the exchange barrier for the decomplexation or bimolecular cation interchange processes. We will come back to this point in the Discussion section.

**Exchange Mechanism.** Two mechanisms can account for the observed exchange, as proposed by Shchori et al.:<sup>9,10</sup> (a) the unimolecular decomplexation



(b) the bimolecular cation interchange mechanism



All species are solvated. Table I shows that for different  $\rho$  ratios and a constant total sodium concentration (0.037 M), the values of the mean lifetime  $(k_A + k_B)^{-1}$  are constant.

In the hypothesis of an unimolecular decomplexation (eq 3),  $k_A + k_B = k_{-1} + k_1[\text{Cr}]$ . Because the measured  $(k_A + k_B)$  is constant,  $k_{-1}$  should be  $\gg k_1[\text{Cr}]$ . Moreover, since the equilibrium constant for the complex formation is large ( $\geq 10^5$ ),<sup>20</sup> then  $k_1/k_{-1}[\text{Cr}] \approx \rho/(1 - \rho)$ . We arrive at an absurd situation for  $\rho \geq 0.5$ , for which the measured rate constant should vary with the total crown concentration. Therefore, the exchange process does not obey the mechanism of eq 3.

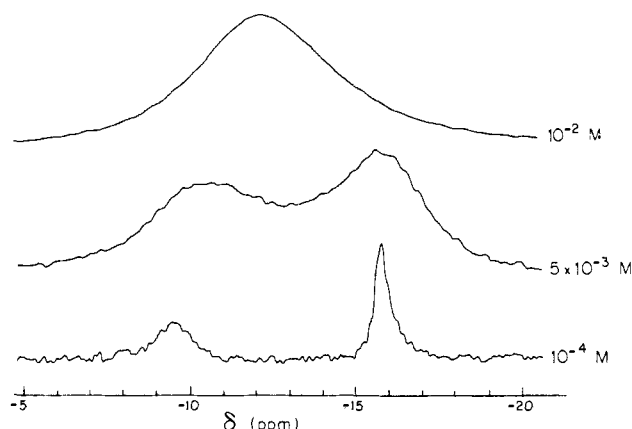
For a bimolecular cation interchange mechanism (eq 4)

$$k_A + k_B = k_2[\text{Na}^+]_T$$

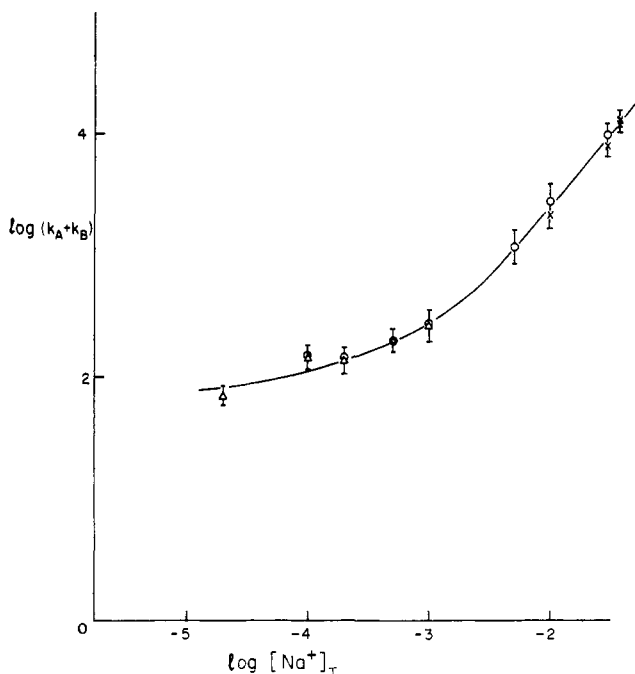
and the constancy of the measured rate constant militates in favor of this mechanism. An obvious test for this mechanism consists of a study of the dependence of rate on Na<sup>+</sup> concentration. Figure 3 shows the Na-23 spectra as a function of the total sodium concentration at 295 K and 79.35 MHz for a ratio  $\rho = 0.50$ . A coalescence is observed at a particular sodium concentration ( $5 \times 10^{-3}$  M). The test confirms the hypothesis of the bimolecular cation interchange mechanism. In order to derive the rate constants from these spectra, a complete line-shape analysis has been carried out by using the Bloch equations modified for an uncoupled spin system undergoing chemical exchange between two non-equivalent sites.<sup>22</sup> Figure 4 shows the variation of the calculated  $k_A + k_B$  as a function of the total sodium concentration. At higher

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**Figure 3.** Na-23 NMR spectra at 79.35 MHz of sodium tetraphenylborate solutions in nitromethane, in the presence of DB24C8 ( $[\text{DB24C8}]/[\text{Na}^+] = 0.50$ ) at different sodium concentrations (295 K).



**Figure 4.** Values of  $\log(k_A + k_B)$  as a function of  $\log[\text{Na}^+]_T$ . ( $k_A + k_B$ ) has been calculated by using eq 2 (X), a complete line-shape analysis (O), or a line-shape analysis on the exchange broadened resonance of the solvated sodium ( $\Delta$ ) (see Experimental Section).

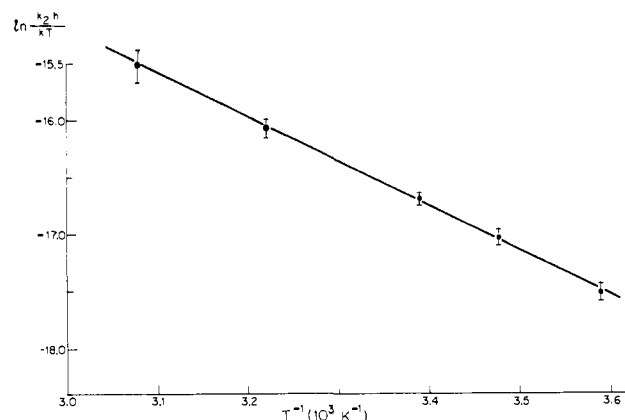
values of  $[\text{Na}^+]_T$ , the relationship is linear and is in perfect agreement with a single mechanism, namely eq 4 with  $k_2 = (2.8 \pm 0.3) \times 10^5 \text{ s}^{-1} \text{ mol}^{-1} \text{ L}$  (295 K). At lower concentrations of  $[\text{Na}^+]_T$  ( $< 10^{-3} \text{ M}$ ), below the coalescence concentration, the relationship is no longer linear and the observed rate constant becomes independent of  $[\text{Na}^+]_T$ . The leveling of the rate constant shows that a residual unimolecular decomplexation mechanism becomes operative at low sodium concentrations ( $5 \times 10^{-4}$  to  $2 \times 10^{-5} \text{ M}$ ). In that concentration region, we can subtract the bimolecular contribution from the measured  $(k_A + k_B)$  value, which gives an approximate value for  $\Delta G^*_{\text{uni}} \approx 65 \text{ kJ mol}^{-1}$  (300 K).

Table II shows the values of  $T_{2,\text{ex}}^{-1}$  ( $= T_{2,\text{obsd}}^{-1} - T_{1,\text{obsd}}^{-1} - T_{2,\text{inh}}^{-1}$ ) and of  $k_A + k_B = k_2[\text{Na}^+]_T$  obtained from eq 2 for a total sodium concentration of 0.037 M and for three different  $\rho$  values (0.30, 0.50, and 0.80). A variation with temperature of the difference in Na-23 chemical shifts between the solvated sodium and the 1:1 complexed sodium has to be taken into account (0.8 Hz/K). Figure 5 shows the linear relationship between  $(\ln k_2 - \ln(kT)/h)$  and  $T^{-1}$ , furnishing the activation parameters for the cation interchange process:  $\Delta H^* = 31 \pm 3 \text{ kJ mol}^{-1}$  and  $\Delta S^* = -32 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$ .

**Table II.** Measured Rate Constants at Different Temperatures for Different  $\rho$  Ratios

$\rho^a$	$T_{2,\text{ex}}^{-1},^b$	$k_A + k_B,^c 10^4 \text{ Hz}$
$T = 324.9 (\pm 0.5) \text{ K}$ ( $\Delta\nu^d = 516 \pm 3 \text{ Hz}$ )		
0.30	$50 \pm 6$	$4.4 \pm 0.6$
0.50	$58 \pm 6$	$4.5 \pm 0.5$
0.80	$41 \pm 7$	$4.1 \pm 0.7$
$T = 310.6 (\pm 0.5) \text{ K}$ ( $\Delta\nu = 507 \pm 3 \text{ Hz}$ )		
0.30	$80 \pm 7$	$2.7 \pm 0.3$
0.50	$102 \pm 8$	$2.5 \pm 0.2$
0.80	$66 \pm 10$	$2.5 \pm 0.4$
$T = 287.5 (\pm 0.5) \text{ K}$ ( $\Delta\nu = 488 \pm 3 \text{ Hz}$ )		
0.30	$205 \pm 14$	$0.96 \pm 0.09$
0.50	$262 \pm 14$	$0.90 \pm 0.06$
0.80	$156 \pm 16$	$0.96 \pm 0.09$
$T = 278.5 (\pm 0.5) \text{ K}$ ( $\Delta\nu = 478 \pm 3 \text{ Hz}$ )		
0.30	$284 \pm 13$	$0.67 \pm 0.04$
0.50	$417 \pm 24$	$0.54 \pm 0.04$
0.80	$233 \pm 13$	$0.62 \pm 0.04$

<sup>a</sup>  $\rho = [\text{crown}]/[\text{sodium}]$ , with  $[\text{Na}^+] = 0.037 \text{ M}$ . <sup>b</sup>  $T_{2,\text{ex}}^{-1} = T_{2,\text{obsd}}^{-1} - T_{2,\text{inh}}^{-1} - T_{1,\text{obsd}}^{-1}$  (see text). <sup>c</sup> Sum of the pseudo-first-order rate constants for the two-sites exchange process ( $k_A + k_B = k_2[\text{Na}^+]_T$ ). <sup>d</sup>  $\Delta\nu = \nu_A - \nu_B$ , the difference of the Na-23 chemical shifts of solvated sodium and 1:1 complexed sodium at different temperatures.



**Figure 5.**  $(\ln k_2 - \ln(kT)/h)$  against  $T^{-1}$ .  $k_2$  has been calculated from eq 2 after correction of the observed  $T_2$  for quadrupolar and inhomogeneity broadenings as determined by  $T_1$  measurements (eq 1).  $[\text{NaBPh}_4] = 0.037 \text{ M}$  in nitromethane;  $[\text{DB24C8}]/[\text{NaBPh}_4] = 0.50$ . Under these conditions, the mechanism is purely bimolecular and  $(k_A + k_B) = k_2[\text{Na}^+]_T$ .

## Discussion

The most important finding of this work is the efficiency of a bimolecular process for the exchange of sodium complexed by the large crown DB24C8. We are forced to admit that a transition state resulting from the close approach of two cationic species is energetically favored compared to a transition state resulting from the partial opening of the wrapped ligand around the cation and its partial release. Nitromethane ( $\text{DN} = 2.8$ )<sup>23</sup> does not compete efficiently with the crown oxygens for the occupancy of the sodium coordination sphere: the 1:1 complex is a wrapped complex<sup>7</sup> and  $(n+1)/n$  complexes are formed.<sup>20</sup> We visualize the transition state for the cation exchange as being close to a 2:1  $\text{Na}^+/\text{DB24C8}$  complex, with a quasi-planar structure in which two groups of four oxygens face the opposite sides of the molecular plane, each group complexing one sodium.<sup>20</sup> The measured activation energy ( $41 \text{ kJ mol}^{-1}$  at 300 K) will then be the result of the balance between conformational changes and stabilization by the second sodium cation. It has been proposed that four trans-to-gauche conformational changes can account for about  $50 \text{ kJ mol}^{-1}$ .<sup>24</sup> In this process, the activation enthalpy necessary for conformational

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changes can be counterbalanced by favorable interactions of the liberated crown oxygens with excess sodium cations in solution, even if this results in a loss of activation entropy ( $\Delta S^\ddagger = -32 \text{ J mol}^{-1} \text{ K}^{-1}$ ). The negative value of  $\Delta S^\ddagger$  is in agreement with a bimolecular process and is indicative of the fact that the associating species are not desolvated to a large extent. This transition state can lead, by further cation desolvation and crown wrapping, to the 1:1 complex, which provides a mechanism for cation exchange inside the wrapped crown or can lead by further solvent and/or counteranion reorganization to the 2:1 complex or higher aggregates. At any stage of the aggregation, the slow step for the process remains the opening of the wrapped 1:1 complex. So, formation of aggregated species does not provide any "fast" way for cation exchange inside the 1:1 complex. Moreover, since the concentration of these species is minor (<2%), their exchange contribution to the observed transverse relaxation rate is negligible. This is what we observe (Figure 2) where the kinetic treatment is applicable for a two-site case. The unimolecular decomplexation mechanism becomes competitive only at low concentrations (< $10^{-3}$  M).  $\Delta G_{\text{uni}}^\ddagger$  can be estimated:  $65 \text{ kJ mol}^{-1}$  at 300 K. The barrier for the unimolecular decomplexation should originate in the same kind of conformational changes of the 1:1 complex than for the associative process. However the extra stabilization afforded by interaction of exposed crown oxygens with the (poorly) solvated sodium, operative in the associative process, is absent in the unimolecular decomplexation process.

In conclusion, we have shown the efficiency of an associative cation interchange mechanism for the complexation-decomplexation reactions of crown ethers. This process is operative for DB24C8 and sodium concentrations higher than  $10^{-3}$  M at 295

K. At lower concentrations, the "classical" unimolecular decomplexation mechanism is operative. We are now pursuing our investigations to define the roles of solvent and counteranion.

### Experimental Section

Origin and purity of the products have been described in the preceding paper<sup>20</sup> in this issue. Na-23 NMR spectra were recorded at 79.35 MHz (Varian XL-300), 52.92 MHz (Varian XL-200), and 21.04 MHz (Varian FT-80). The temperature in the probe was measured with a thermocouple submerged in a nitromethane solution in a nonspinning 10-mm NMR tube. Temperature of the sample was estimated at  $\pm 0.5$  K. No lock was used on the high-field instruments whose field drift was negligible.

For low sodium concentrations (< $10^{-3}$  M), the solvent used was a 5% nitromethane- $d_3$  in nitromethane solution and a deuterium lock was used. Pulse widths of  $90^\circ$  were  $22.5 \mu\text{s}$  (79.35 MHz) and  $20 \mu\text{s}$  (52.92 MHz).

Spectrum analysis was carried out by using an optimization Simplex procedure<sup>25</sup> on a complete line-shape analysis.<sup>22</sup> In the case of the moderately rapid exchange, the rate constant could be calculated with eq 2, giving the same results as the ones obtained through the optimization procedure (see Figure 2).

**Acknowledgment.** We gratefully acknowledge Natural Science and Engineering Research Council of Canada (NSERCC) and Research Corp. for financial support. H.D.H.S. acknowledges NSERCC for a postgraduate scholarship, and A. D. acknowledges NATO for a travel grant.

**Registry No.** Na, 7440-23-5.

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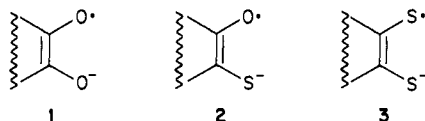
## Spin Probes Derived from Dithiols<sup>1</sup>

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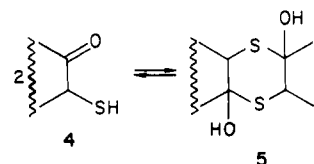
**Abstract:** Mono- and dithio-1,2-semidiones have been prepared. The dithiosemidiones have lower  $a_\alpha^H$  and higher  $g$  values than the semidiones. The dithiete, 1,4-dithiin, and 2,3-dihydro-1,4-dithiin radical cations derived from bicyclo[2.2.1]hept-2-ene-2,3-dithiol have been prepared and demonstrated to possess a strong W-plan interaction with the  $7_{\text{anti}}$ - and  $5,6_{\text{exo}}$ -hydrogen atoms as expected for a symmetric SOMO. The radical cation of 2,3-dithiabicyclo[2.2.1]heptane has an antisymmetric SOMO, and the long-range interaction with the  $7_{\text{anti}}$ -hydrogen atom is not observed. 2,5-Dithiabicyclo[4.2.1]non-3-ene radical cation possesses a symmetric SOMO, and long-range splitting is observed at the anti position of the methylene bridge. 1,2-Dithietane and 1,2-dithiolane radical cations have been prepared, and the surprising values of  $a_\alpha^H$  of 3.7 and 10 G, respectively, discussed in terms of an antisymmetric SOMO. 2,3-Dihydro-1,4-dithiin radical cations exist in a half-chair conformation with nonequivalent quasi-equatorial and quasi-axial hydrogen atoms. For the 5,6-dimethyl derivative  $\Delta H^\ddagger = 2.3 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -20 \text{ eu}$  were measured in  $\text{H}_2\text{SO}_4$  with a coalescence temperature of  $70^\circ \text{C}$ .

**Radical Anions.** We have investigated the effect on spin distribution and ESR parameters ( $a_\alpha^H$ ,  $g$  value) of replacing 1,2-semidione oxygen atoms by sulfur atoms ( $1 \rightarrow 2 \rightarrow 3$ ). Mo-



nothiosemidiones were synthesized from the  $\alpha$ -mercapto ketones

4 or their cyclic dimers 5, by treatment with  $\text{Me}_3\text{CO}^-\text{K}^+$  in  $\text{Me}_2\text{SO}$  (Scheme I).



In certain cases, dithiosemidiones 3 could be prepared by treatment of thiophosphoric esters of enedithiols 7 with  $\text{Me}_3\text{CO}^-\text{K}^+$  in  $\text{Me}_2\text{SO}$  (reaction 1). This procedure worked for the thiophosphoric esters derived from bicyclo[2.2.1]heptane-2,3-dione, camphorquinone, or bicyclo[2.2.2]octane-2,3-dione but failed for

(1) Aliphatic Semidiones. 44. This work was supported by Grants CHE-7823866 and CHE-8119343 from the National Science Foundation. For a preliminary communication, see: Russell, G. A.; Zaleta, M. *J. Am. Chem. Soc.* 1982, 104, 2318.