

essentially equal to the limiting values δ_B and $1/T_{2B}$ for $R_0 \geq 1.50$ even at the highest temperatures studied. At lower temperatures complexation is essentially complete at all values of R_0 . Complexation of $\text{Na}^+(\text{solv})$ with 15C5 is not complete at any temperature or R_0 value used; however, p_B is 0.96 at the lowest temperature and largest R_0 value ($R_0 = 13.0$).

For 18C6 the exchange rate is slow at the lowest temperatures for $R_0 < 0.7$. For R_0 in the range from 0.7 to 1.0 at lower temperatures, the exchange rate is intermediate. The low-temperature data for which $R_0 < 0.7$ were used to determine values of ΔH_1^\ddagger and ΔS_1^\ddagger of 1.1 kcal mol⁻¹ and -18 cal mol⁻¹ K⁻¹, respectively. The activation enthalpy is similar to that expected for simple solvent exchange and considerably smaller than the values reported by other authors for complexation of $\text{Na}^+(\text{solv})$ by the more rigid, substituted 18-crown-6 complexes in other solvents.¹⁷ As 18C6 is more flexible than the substituted 18C6 species, it may more easily complex $\text{Na}^+(\text{solv})$ and require a smaller activation enthalpy.

The activation entropies for complexation, ΔS_1^\ddagger , and decomplexation, ΔS_{-1}^\ddagger , are -18 and -13 cal mol⁻¹ K⁻¹, respectively. Activation entropies determined from previous studies with substituted crown ethers are negative for complexation and positive for decomplexation.¹⁷ Possibly the greater flexibility of 18C6 allows for a more ordered transition state.

The activation energies for relaxation of Na^+C for 18C6 and 15C5 are not significantly different and are considerably larger than expected for a solvent reorientation relaxation mechanism but are of the right magnitudes for relaxation by rotational diffusion of the Na^+C (or $\text{Na}^+\text{C}, \text{Br}^-$) species.

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Registry No. Na, 7440-23-5; NaBr, 7647-15-6; 18-crown-6, 17455-13-9; 15-crown-5, 33100-27-5.

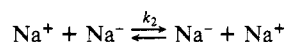
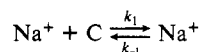
Sodium-23 Nuclear Magnetic Resonance Study of Sodium Metal in Methylamine Solutions That Contain 18-Crown-6. Kinetics of Sodium Cation-Solide Ion Exchange

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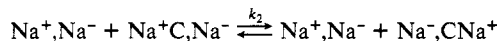
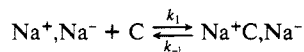
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Sodium-23 NMR spectra of Na^+ -18-crown-6, $\text{Na}^+(\text{Na}^+\text{C}, \text{Na}^-)$ solutions in methylamine were studied as functions of temperature and mole ratio of crown ether to sodium. A broad band of Na^+C and a narrow band of Na^- were observed at low temperatures, but coalesced into a single band at -6 to +5 °C depending upon the ratio of dissolved sodium to free crown ether and exhibited exchange narrowing as the temperature was increased further. Although the data could be quantitatively fit to the simple mechanism



the ionic species probably exist largely as ion pairs at the concentrations used. A modified mechanism that fit the data was



in which the first equilibrium involves cation complexation but no electron exchange while the second involves exchange of Na^+C with Na^- . Neither cation-anion exchange within the ion pairs Na^+, Na^- and $\text{Na}^+\text{C}, \text{Na}^-$ nor cross exchange between two $\text{Na}^+\text{C}, \text{Na}^-$ species contributed significantly to the exchange rate. Exchange broadening of the Na^- band was used to determine the apparent rate constant $k_2/K_1 = (1.0 \pm 0.2) \times 10^5 \text{ s}^{-1}$ at 25 °C with $\Delta H^\ddagger_{\text{app}} = 19 \pm 1 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger_{\text{app}} = 27 \pm 3 \text{ cal mol}^{-1} \text{ K}^{-1}$. By using the value of K_1 obtained for NaBr solutions in methylamine, we calculated approximate values of $k_2 = (2.4 \pm 0.8) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $\Delta H_2^\ddagger = 14 \pm 4 \text{ kcal mol}^{-1}$, and $\Delta S_2^\ddagger = 22 \pm 6 \text{ cal mol}^{-1} \text{ K}^{-1}$. Several unsuccessful attempts were made to obtain similar data with sodium and 15-crown-5. Although broad Na^+C and narrow Na^- bands were observed at low temperatures, rapid decomposition prevented study of the exchange kinetics in this case.

Introduction

Previous ²³Na studies have been made with sodium metal solutions that contain either cryptand [2.2.2], (C222),^{1,2} 18-crown-6, (18C6),^{2,3} or 15-crown-5, (15C5).³ The crown ether data were obtained in methylamine solutions whereas three different solvents including methylamine were used for the cryptand studies. The

low-temperature NMR spectrum for each of these systems consists of a broad band associated with the Na^+ -ligand complex (Na^+C) and a narrow band associated with Na^- . Edwards and co-workers have observed the Na^- band in solutions prepared from Na metal and either hexamethylphosphoric triamide⁴ or *N,N*-diethylacetamide⁵ in the absence of any complexing agent. In all cases the

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Na^+ band is very narrow and its chemical shift is independent of the solvent and complexing agent used.

The crown ether solutions are of particular interest since the two bands observed at low temperatures broaden and collapse into a single band as the temperature is increased.² Presumably, this does not occur in cryptand solutions because the exchange of Na^+ between the cryptand and solvent or between the cryptand and Na^+ is very slow.⁶ The variable-temperature studies that were done with the crown ether solutions^{2,3} indicated that exchange parameters and possibly the exchange mechanism for electron exchange could be obtained by carrying out quantitative studies of the effect of crown ether concentration on the NMR spectra.

One of the proposed exchange mechanisms includes the rate of complexation-decomplexation of $\text{Na}^+(\text{solv})$ by the crown ether.² It appears that the determination of the kinetic parameters for electron exchange in metal solutions depends on an independent determination of the complexation constant and/or kinetic parameters in salt solutions. Two such studies have been done.^{3,7} The complexation constant for 18C6 solutions varies from approximately 220 to 47 000 M^{-1} in the temperature range from +25 to -94°C ⁷ while for 15C5 solutions it varies from 5 to 60 M^{-1} over the same temperature range.⁷ On the basis of these complexation constants, 15C5 does not appear to be a suitable complexing agent for dissolving appreciable concentrations of sodium in methylamine. The ^{23}Na NMR spectra reported by Andrews³ for Na-15C5 solutions in methylamine indicated that the solutions were partially decomposed and that the solubility of sodium was low in the presence of 15C5. This paper confirms these observations and presents quantitative data for Na^+-Na^- exchange rates in methylamine in the presence of 18C6.

Experimental Section

Purification of most reagents, preparation of solutions, and other experimental procedures are described elsewhere.⁷ A sealed tube of predistilled sodium metal in Pyrex was added to an open-ended arm of an apparatus equipped with a calibrated graduated cylinder and a precision 10-mm-o.d. NMR tube. The open end was then attached with heat-shrinkable Teflon tubing to a short Pyrex tube sealed at one end. The apparatus was evacuated ($\sim 10^{-5}$ torr), and the sealed tube of sodium was broken and moved into the side arm which was then sealed off under vacuum. The sodium was then distilled into an approximately 3-cm-o.d. bulb attached to the same arm of the apparatus. The vessel was then transferred to an inert-atmosphere box, and a weighed amount of crown ether was added. After evacuation, a measured volume (~ 3 mL) of purified methylamine was distilled into the graduated cylinder and the apparatus was transferred to a cooled 2-propanol bath (-20°C). The crown ether solution was poured back and forth between the bulb with the sodium mirror and the graduated cylinder until all or nearly all of the metal had dissolved, then poured into the NMR tube, frozen, and removed by making a vacuum seal-off. When some metal remained undissolved, the amount was determined by a pH titration after the metal had been allowed to react with water.

Both a Varian DA-60 spectrometer (sodium frequency 15.871 MHz), modified for FT operation, and a Bruker WH-180 spectrometer (47.61 MHz) were used to obtain ^{23}Na spectra. The sweep widths used were generally at least 5 times the line widths. At temperatures for which both the Na^+C and Na^- bands were resolvable, data were collected at two different sweep widths, typically 1 KHz and relatively few pulses for the Na^- band and 20 KHz and relatively many pulses for the Na^+C band. Chemical shifts and line widths were measured as previously described.⁷

The weighted nonlinear least-squares program KINFIT^{4,8} and either a CDC-6500 or CDC-7501 computer were used to fit the appropriate equations to the experimental chemical shifts and

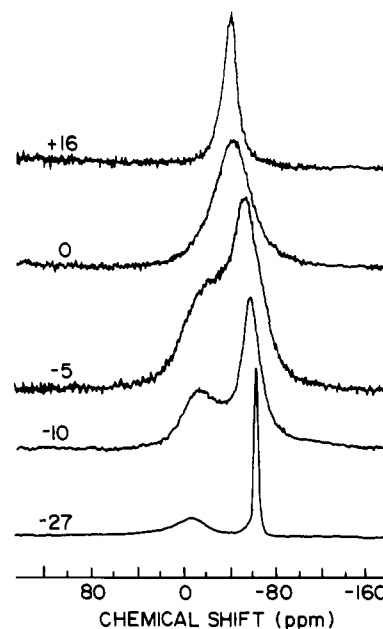


Figure 1. ^{23}Na NMR spectra of a solution with $R_0 = 1.52$ as a function of temperature.

relaxation rates. These computers were also used to simulate NMR spectra over the entire exchange region by using the complete Bloch-McConnell equations.⁹

Results and Discussion

Solutions That Contain 18C6. The ^{23}Na NMR chemical shifts and relaxation rates were measured as functions of temperature for four different crown ether and sodium concentrations. Since the major ionic species are Na^+C and Na^- , the appropriate crown to sodium ratio in this case is

$$R_0 = 2[\text{C}]_0/[\text{Na}]_0 \quad (1)$$

in which $[\text{C}]_0$ and $[\text{Na}]_0$ are the initial molar concentrations of 18-crown-6 and sodium metal, respectively. Typical spectra at various temperatures are shown in Figure 1. The chemical shifts and transverse relaxation times as functions of temperature are shown in Figures 2-5.

At low temperatures the spectrum corresponds to separate Na^+C and Na^- bands. The Na^- band becomes exchange broadened at higher temperatures before the two bands merge into a single band. The chemical shift of the Na^- band is temperature independent at lower temperatures but approaches that of the single merged band as the temperature increases. The average chemical shift of all the data in the temperature-independent region is -62.2 ± 0.3 ppm (-61.8 ppm relative to an infinitely dilute NaCl aqueous solution), which indicates that the shift lacks a significant paramagnetic component. The value agrees with the chemical shift of Na^- reported by other authors¹⁻⁵ and is very nearly the same as that calculated for a gaseous Na^- ion.²

The Na^- band is extremely narrow, and the corrected line width of 1-3 Hz is temperature independent at the lower temperatures. Both the chemical shift and the relaxation rates of Na^- indicate that this ion is not greatly perturbed by the solvent. Apparently, the two outer s electrons shield the p electrons from strong interactions with the solvent. In addition, the large size of Na^- minimizes quadrupolar broadening.

At temperatures for which the Na^+C band is not too broad and exchange broadening is not too large, it is possible to obtain a reasonably intense spectrum of both bands (see Figure 1). For these spectra it was possible to integrate both bands. The area under the Na^+C band was consistently somewhat lower than that of the Na^- band (20%-30%). It is likely, however, that the two areas would be equal if correction could be made for the loss of intensity of the very broad Na^+C band in base line noise and by

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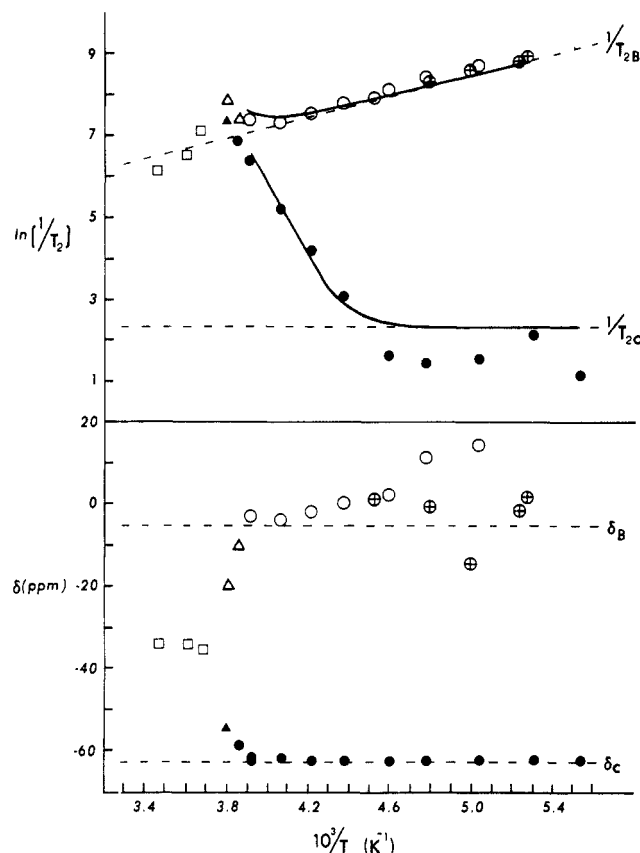


Figure 2. Chemical shifts (lower) and relaxation rates (upper) for $R_0 = 1.37$: \circ , Na^+C ; \bullet , Na^- ; Δ and \blacktriangle , for Na^+C and Na^- that are strongly overlapped and may not have Lorentzian line shapes; \square , exchange averaged band; \oplus , data obtained at 47.61 MHz. The solid lines were calculated from the parameters given in Table I.

the delay times required (typically 100 μs).

The NMR properties of Na^+ , Na^+C , and Na^- are probably not very sensitive to the formation of solvent-separated or crown-ether-separated ion pairs. The concentration dependence of the exchange rate will, however, be strongly dependent on the state of ionic aggregation. Since in this work the lowest sodium concentration studied was 0.136 M, it is almost certain that the ionic species are ion-paired. We estimate, for example, from the conductivity data of Dewald and Browall¹⁰ that the ion-pair formation constant of Na^+Na^- is $\sim 10^3$. Although the complexation of cations by crown ethers or cryptands can prevent contact ion-pair formation, it does not prevent the formation of "loose" or complexant-separated ion pairs. Indeed, ion-pair formation constants are not strongly affected by complexation in solvents which favor solvent-separated ion pairs.¹¹⁻¹³ We must therefore conclude that the predominant species in the solutions studied in this work are excess crown ether and Na^+C , Na^- with small concentrations of Na^+ , Na^- produced by dissociation of Na^+C , Na^- .

The presence of paramagnetic solvated electrons in a methylamine solution that contained sodium metal and 18C6 has been observed by using EPR.¹¹ These EPR spectra were obtained in the temperature range from -46 to -4 $^\circ\text{C}$ which is the approximate range of exchange broadening of the Na^- band. The intensity of the electron EPR signal was very small at the lowest temperature and increased nearly linearly with increasing temperature. Based upon our data the solvated electron concentration must be small compared with the concentration of Na^- since the areas of the Na^+C and Na^- bands are nearly equal. The existence of even a relatively small concentration of a paramagnetic species could have a large effect on the exchange rate, however, so that the presence of solvated electrons cannot be ignored.

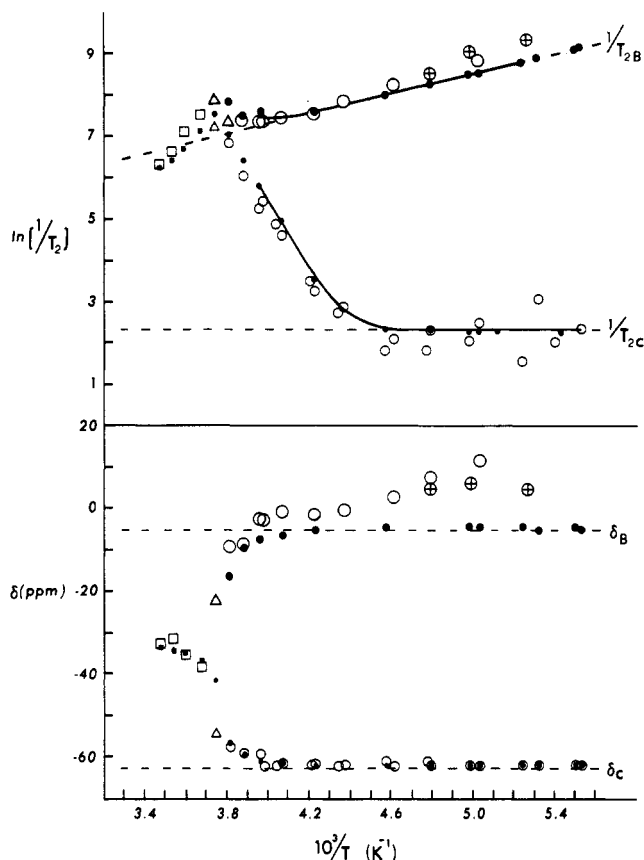
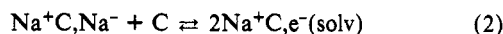


Figure 3. Chemical shifts (lower) and relaxation rates (upper) for $R_0 = 1.52$: open symbols represent the experimental data; \oplus , data obtained at 47.61 MHz. Solid symbols were obtained from simulated spectra. The solid lines were calculated from the parameters given in Table I.

The relative concentration of solvated electrons increases as the mole ratio R_0 increases because of the reaction



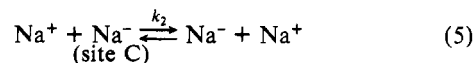
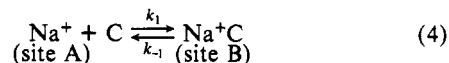
If the exchange mechanism included solvated electrons as important intermediates, the rate would increase with R_0 . In fact, the opposite behavior is observed: increasing R_0 results in slower exchange rates and higher coalescence temperatures.

Since the solubility of sodium in methylamine is very low in the absence of complexant, the concentration of free 18C6 is given by

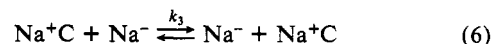
$$[\text{C}] = [\text{C}]_0 - [\text{Na}]_0/2 \quad (3)$$

As shown in Figure 6, the coalescence temperature depends only on the ratio $[\text{Na}]_0/[\text{C}]$. In fact, the exchange rate at a given temperature is directly proportional to this ratio.

If one could ignore ion-pair formation, the simple mechanism



would fit the data very well. A small additional contribution proportional to $[\text{Na}]_0$ that might originate from the direct exchange reaction



could not be completely ruled out, but the uncertainty in the value of k_3 was nearly as large as the value itself.

If we acknowledge that most of the ionic species are present as ion pairs, certain direct exchange pathways are excluded. For example, eq 5 gives a direct dependence of the rate on $[\text{Na}]_0$ that would disappear if exchange of Na^+ and Na^- in the ion pair, Na^+Na^- , could occur rapidly. Similarly, the simple exchange

(10) Dewald, R. R.; Browall, K. W. *J. Phys. Chem.* **1970**, *74*, 129.

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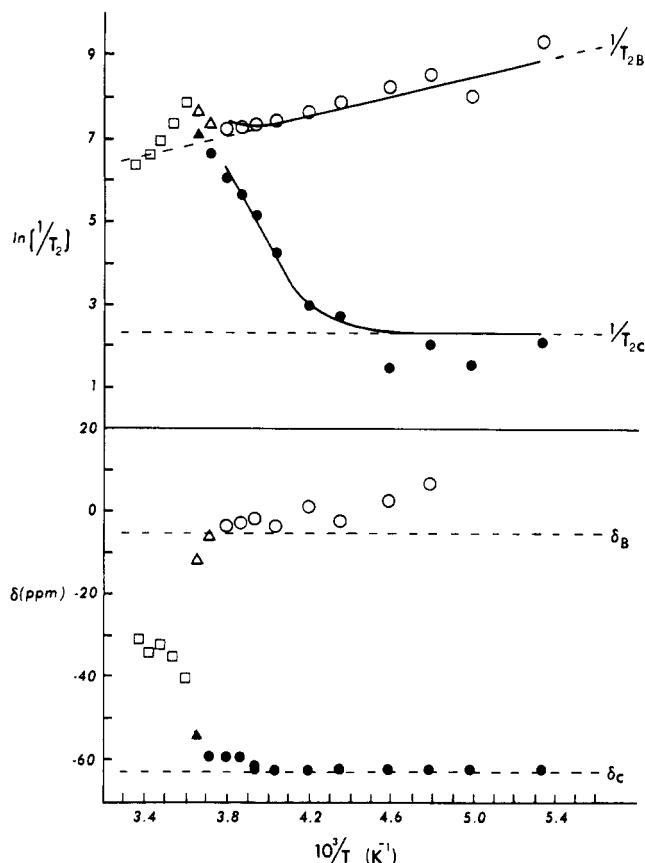


Figure 4. Chemical shifts (lower) and relaxation rates (upper) for $R_0 = 2.62$. See the legend of Figure 2 for the definition of symbols.

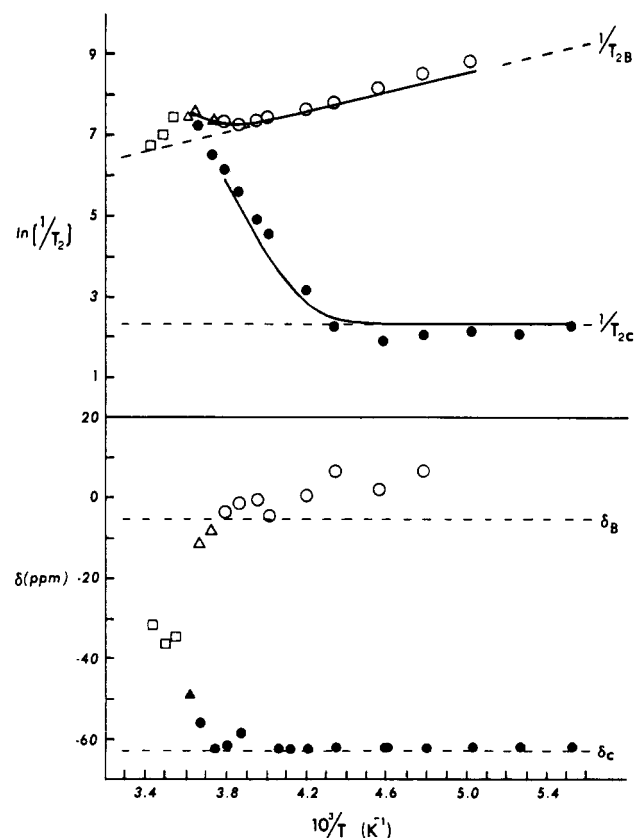


Figure 5. Chemical shifts (lower) and relaxation rates (upper) for $R_0 = 3.22$. See the legend of Figure 2 for the definition of symbols.

of Na^+C with Na^- in the ion pair, $\text{Na}^+\text{C}, \text{Na}^-$, would yield an additive concentration-independent term to the rate. Other possible exchange processes that give the wrong concentration

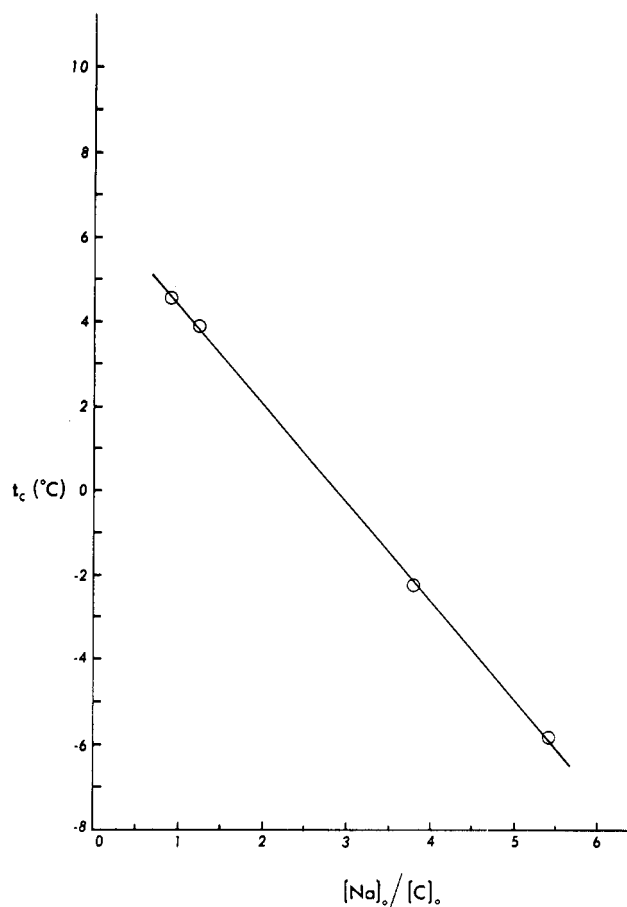
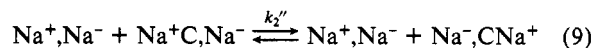
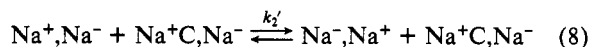
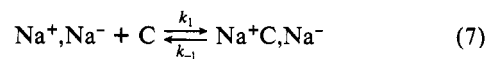


Figure 6. Coalescence temperature as a function of $[\text{Na}]_0/[\text{C}]$.

dependence are the following: (1) the exchange of Na^+ between the ion pairs Na^+, Na^- and $\text{Na}^+\text{C}, \text{Na}^-$; (2) the exchange of Na^+ with Na^- simultaneous with the exchange of Na^- with Na^+C by the reaction of Na^+, Na^- with C ; (3) the exchange of Na^+C with Na^- by the bimolecular reaction of two complexed ion pairs, $\text{Na}^+\text{C}, \text{Na}^-$; and (4) the exchange of Na^+ with Na^- by the bimolecular reaction of two ion pairs, Na^+, Na^- . Although all of these pathways might contribute to the observed exchange rate, they cannot provide dominant exchange pathways.

The only scheme compatible with the observed rate law which also recognizes the dominant role of ion pairing is a modification of eq 4 and 5 to include ion pairs. The resulting mechanism is



Reaction 7 involves exchange of Na^+ (site A) in Na^+, Na^- with Na^+C (site B) by complexation of the cation. It does not involve exchange of Na^- . Reactions 8 and 9 are "crown-ether-assisted electron-pair-transfer" reactions that involve the exchange of Na^+ (site A) and Na^- (site C) in the ion pair Na^+, Na^- (reaction 8) and/or the exchange of Na^+C (site B) and Na^- (site C) in $\text{Na}^+\text{C}, \text{Na}^-$ (reaction 9). Both exchange reactions 8 and 9 could also occur simultaneously in a single bimolecular step. By noting that $[\text{Na}^+\text{C}, \text{Na}^-] = [\text{Na}]_0/2$ and that $[\text{Na}^+, \text{Na}^-] \approx (k_{-1}/2k_1) \cdot ([\text{Na}]_0/[\text{C}])$, we obtain (see Appendix)

$$1/\tau_A = k_1[\text{C}] + k_2'[\text{Na}]_0 \quad (10)$$

$$1/\tau_B = k_{-1} + \frac{k_2''[\text{Na}]_0}{K_1[\text{C}]} \quad (11)$$

$$1/\tau_C = \frac{(k_2' + k_2'')[\text{Na}]_0}{1 + K_1[\text{C}]} \approx \frac{(k_2' + k_2'')[\text{Na}]_0}{K_1[\text{C}]} \quad (12)$$

TABLE I: Kinetic Parameters for Sodium Cation and Anion Exchange in Methylamine Solutions That Contain Sodium and 18C6

mechanism ^a	$10^{-5}k_{\text{app}},^d \text{ s}^{-1}$	$10^{-5}k_3,^d \text{ s}^{-1}$	$\Delta H_{\text{app}}^*, \text{ kcal mol}^{-1}$	$\Delta S_{\text{app}}^*, \text{ cal mol}^{-1} \text{ K}^{-1}$	$\Delta H_3^*, \text{ kcal mol}^{-1}$	$\Delta S_3^*, \text{ cal mol}^{-1} \text{ K}^{-1}$	$\sigma(1/T_2),^b \text{ s}^{-1}$
I	1.0 (2)		19 (1)	27 (3)			12.0
II	0.4 (2)	1.0 (8)	17 (2)	20 (6)	14 (4)	12 (9)	9.7

^a Mechanism for chemical exchange; see eq 7–9 for mechanism I. Mechanism II includes also the direct exchange reaction between two $\text{Na}^+\text{C}, \text{Na}^-$ species. ^b Linear estimate of the standard deviation of the relaxation rates. ^c Standard deviation estimate of the last digit is given in parentheses. ^d At 25 °C.

Because Na^+, Na^- is a minor species, this three-site problem can be reduced to an effective two-site model that involves only a single relaxation time, τ , defined by either

$$1/\tau = 1/\tau_B - \tau_A/(\tau_{AB}\tau_{BA}) \quad (13)$$

or

$$1/\tau = 1/\tau_C - \tau_A/(\tau_{AC}\tau_{CA}) \quad (14)$$

in which τ_{ij} is the time that a sodium nucleus resides in site i before transferring to site j (see Appendix). For the model described by eq 7–9 this gives

$$\frac{1}{\tau} = \frac{k_{-1}[\text{Na}]_0(k_2' + k_2'')}{k_1[\text{C}] \left[1 + \frac{k_2'[\text{Na}]_0}{k_1[\text{C}]} \right]} \quad (15)$$

Comparison of the Na^- to Na^+ exchange rate observed here with the Na^+C to Na^+ exchange rate observed with Br^- as the counterion⁷ shows that $k_2' \ll k_1$. By noting that $[\text{Na}]_0$ and $[\text{C}]$ are of comparable magnitude, we can reduce eq 15 to

$$\frac{1}{\tau} = \frac{(k_2' + k_2'')[\text{Na}]_0}{K_1[\text{C}]} = \frac{k_2[\text{Na}]_0}{K_1[\text{C}]} = k_{\text{app}} \frac{[\text{Na}]_0}{[\text{C}]} \quad (16)$$

in which k_2 is a single “effective” rate constant for electron-pair exchange caused by the bimolecular reaction between Na^+, Na^- and $\text{Na}^+\text{C}, \text{Na}^-$ (mechanism I). If the bimolecular reaction of two $\text{Na}^+\text{C}, \text{Na}^-$ species also gives electron-pair exchange, the term $k_3[\text{Na}]_0$ must be added to $1/\tau$ (mechanism II).

The net transverse relaxation times for Na^+C and Na^- in the slow-exchange region are given by

$$\left(\frac{1}{T_2'} \right)_B = \frac{1}{T_{2B}} + \frac{1}{\tau} \quad (17)$$

and

$$\left(\frac{1}{T_2'} \right)_C = \frac{1}{T_{2C}} + \frac{1}{\tau} \quad (18)$$

in which $1/T_{2B}$ and $1/T_{2C}$ are the relaxation rates at sites B and C in the absence of exchange.

The experimental values of $(1/T_2')_C$ for the exchange-broadened Na^- band as functions of temperature and concentration were fit by both eq 16 (mechanism I) and a modified rate equation (mechanism II) that includes the additional term $k_3[\text{Na}]_0$. The kinetic parameters obtained by these procedures are given in Table I. A constant relaxation rate, $1/T_{2C}$, was used as a parameter in the curve-fitting process. The adjusted value of $10 \pm 2 \text{ s}^{-1}$ may be compared with the experimental value of $8 \pm 4 \text{ s}^{-1}$ determined from the low-temperature line widths of the Na^- band. The latter value has a large uncertainty because the field inhomogeneity correction is a substantial percentage of the total line width and tends to overcompensate for the “true” correction. The exchange rate parameters are, however, not very sensitive to the value of $1/T_{2C}$ used.

Mechanism II fit the data somewhat better than mechanism I (see the linear estimate of the standard deviation of the relaxation rates given in Table I). In addition, plots of $1/[\text{Na}]_0\tau$ vs. $1/[\text{C}]$ at various temperatures are linear (but with considerable scatter) and have nonzero intercepts that increase with increasing temperature as required by mechanism II. However, the error in the

TABLE II: Coalescence Temperatures for Methylamine Solution That Contain Sodium and 18C6

sample	$[\text{Na}]_0, \text{ M}$	R_0	$[\text{Na}]_0/[\text{C}]^a$	$t_C,^b \text{ }^\circ\text{C}$	$10^{-4}/\tau,^c \text{ s}^{-1}$
1	0.136	1.37	5.42	−5.8	12.5
2	0.200	1.52	3.82	−2.2	8.82
3	0.234	2.62	1.24	+3.9	2.86
4	0.158	3.21	0.903	+4.6	2.08

^a The equilibrium concentration of 18C6 is given by $[\text{C}] = [\text{C}]_0 - [\text{Na}]_0/2$. ^b The coalescence temperatures were estimated from $\ln(1/T_2)$ vs. $1/T$ plots; see Figures 2–5. ^c Chemical exchange rate for mechanism I; see eq 16. ^d At 25 °C.

rate constant k_3 is nearly as large as that constant. Since the uncertainty in k_3 is too large to conclusively choose mechanism II over I, in all subsequent considerations only mechanism I will be used.

The correlation times calculated from the relaxation rates of the exchange-broadened Na^- band were used with eq 17 to give $1/T_{2B} = 700 \pm 50 \text{ s}^{-1}$ at 25 °C and an activation energy $E^* = 2.4 \pm 0.1 \text{ kcal mol}^{-1}$ for relaxation in site B (Na^+C) in the absence of exchange. This activation energy is not much greater than that expected for solvent reorientation about the Na^+ ion and is significantly smaller than the values reported for NaBr and NaI solutions ($E^* \sim 3.2 \text{ kcal mol}^{-1}$).^{3,7} The origin of this difference is not understood, but it is well outside of experimental error. Evidently the relaxation process for Na^+C with Na^- as a counterion is different from that with Br^- or I^- as counterions.

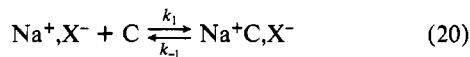
The Bloch-McConnell equations⁹ were used to simulate NMR spectra at all temperatures for one of the solutions, and the results are shown in Figure 3. The parameters used in that simulation, τ , $1/T_{2B}$, E^* , and $1/T_{2C}$, were determined by the curve-fitting procedure described above. The experimental values $\delta_C = -62.2 \pm 0.3 \text{ ppm}$ for metal solutions and $\delta_B = -4.8 \pm 0.5 \text{ ppm}$ for NaBr solutions⁷ were also used. As can be seen from Figure 3, the chemical shifts and relaxation rates determined from simulated spectra generally agree well with the experimental values except that the experimental chemical shifts of the Na^+C band at low temperatures become more paramagnetic with decreasing temperature, while the shifts determined from simulated spectra are temperature independent. The fact that the lower temperature chemical shifts consistently increase with decreasing temperature might indicate that another dynamic process is occurring. This possibility does not appear to be compatible with the lower temperature relaxation rates as any dynamic process that affects the chemical shifts would probably affect the relaxation rates as well. It is likely that a large apparent paramagnetic shift results from a systematic experimental error. The lower temperature spectra of Na^+C and Na^- were obtained under different conditions (see Experimental Section). The presence of the very intense Na^- band made phasing of the Na^+C band very difficult. At the sweep widths used, misphasing of the band can lead to large errors in the chemical shift. Some of the lower temperature data (see Figures 1 and 2) were collected with a Bruker WH-180 spectrometer that has a much larger dynamic range than the modified Varian DA-60 instrument. This made it easier to phase the Na^+C band, and the chemical shifts were not as paramagnetically shifted in these cases. Because the chemical shifts of the Na^+C band apparently do not attain a limiting value at low temperatures, it was necessary to use the value of δ_B that was obtained from NaBr studies⁷ in the spectral simulations. Fortunately, these simulations are not highly sensitive to the particular value of δ_B used.

The coalescence temperatures, t_c , were estimated from the data (see Table II). The condition for coalescence is qualitatively given by

$$1/\tau \sim |\omega_B - \omega_C| \quad (19)$$

where ω_B and ω_C are the chemical shifts in rad s^{-1} for sites B and C, respectively. If k_2/K_1 does not change appreciably, that is, if the temperature range is small, t_c should decrease linearly with increasing $[\text{Na}]_0/[\text{C}]$ (see eq 16 and 19). The expected linear dependence is experimentally verified as shown in Figure 6.

The nature of the Na^+C complex ion is assumed to be similar for both metal and NaBr solutions so that the association constants for the complexation reactions



in which X^- is either Br^- or Na^- are comparable. The results for salt solutions indicate that the complexation constant is not very sensitive to the counterion.^{7,12,13} If this assumption is valid, the complexation constant previously determined⁷ may be used to evaluate the rate constant k_2 from the experimental value of k_{app} . At 25 °C the values of K_1 and k_{app} are $220 \pm 80 \text{ M}^{-1}$ and $(1.0 \pm 0.2) \times 10^5 \text{ s}^{-1}$, respectively. This gives $k_2 = (2.4 \pm 0.8) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C. By using the values of ΔH_1° and ΔS_1° from the previous study⁷ and $\Delta H_{\text{app}}^\circ$ and $\Delta S_{\text{app}}^\circ$ from this work, ΔH_2° and ΔS_2° were found to be $14 \pm 4 \text{ kcal mol}^{-1}$ and $22 \pm 6 \text{ cal mol}^{-1} \text{ K}^{-1}$, respectively. These results are reasonable since it is expected that the transition state should involve reordering of the solvent and the complexant in the vicinity of the ions involved.

Solutions That Contain 15C5. Previous studies with methylamine solutions that contained NaBr and 15C5 indicated that the complexation constant between $\text{Na}^+(\text{solv})$ and 15C5 is small at all temperatures (+20 to -94 °C).⁷ There is also no evidence of sandwich complex formation, Na^+C_2 , as found in other systems.^{12,13} Such a low complexation constant indicates that 15C5 is not likely to enhance the solubility of sodium metal in methylamine to a large extent. However, both the Na^+C and Na^- bands have previously been observed in methylamine solutions that contain 15C5 and Na^+ .³ In addition, the complexation constant might be different for metal solutions than for salt solutions. Because of these factors, we attempted to study the system in more detail.

Upon the addition of a methylamine-15C5 solution to a sodium mirror a blue solution developed quickly. However, many hours were required to completely dissolve the metal and the dissolution was accompanied by decomposition. The NMR spectra at low temperatures consisted of separate Na^+C and Na^- bands, but the area of the Na^+C band was much larger than that of the Na^- band, confirming the presence of extensive decomposition and obscuring the coalescence temperature.

The broadening of the Na^- band yielded an approximate activation energy of 15 kcal mol^{-1} for the exchange process with $1/\tau \approx 10^5 \text{ s}^{-1}$ at 25 °C and a coalescence temperature of ≈ -23 °C. In view of the extensive decomposition no further information could be obtained about the relaxation rates of Na^+C or Na^- or about the exchange mechanism.

Conclusions

At the time these data were obtained it was surprising that the apparent exchange rates of Na^+ and Na^- were so small and that the rate-limiting step was the electron-pair exchange rather than decomplexation. Edwards and co-workers,^{4,5} however, have recently observed narrow Na^- bands in HMPA and *N,N*-diethylacetamide in the absence of a complexant. The line width of the Na^- band in HMPA at +1 °C, 10 Hz, requires that the rate constant for exchange with Na^+ cannot be larger than 10^2 – $10^3 \text{ M}^{-1} \text{ s}^{-1}$. The exchange rate constant found in the present study

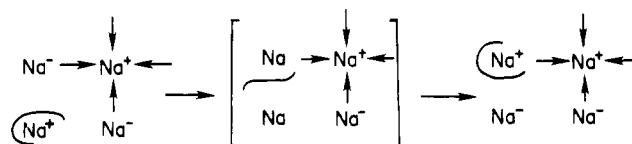


Figure 7. Schematic diagram of a possible pathway for crown-ether-assisted electron-pair transfer. The arrows about Na^+ represent solvent dipoles, and the crown ether is represented by the curved line.

at this temperature is about $10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the bimolecular reaction of Na^+, Na^- with $\text{Na}^+\text{C}, \text{Na}^-$. The contribution to the rate from direct exchange of Na^+ and Na^- in the ion pair is at least an order of magnitude smaller. We conclude, therefore, that simple electron-pair exchange between Na^+ and Na^- in solution is a very slow process, probably because of the extensive solvent reorganization that would be required to form a symmetric transition state. This suggests that the faster exchange observed in our system is facilitated by the presence of the crown ether complex. We expect both Na^- and Na^+C to be only weakly solvated. A symmetric transition state can be visualized as indicated in Figure 7 which does not require substantial solvent reorganization. This pathway involves transfer of the crown ether molecule from Na^+C to Na^- while an electron pair is transferred in the reverse direction. If this is indeed the major pathway for electron-pair transfer, $k_2' \ll k_2''$ so that the "effective" rate constant k_2 is k_2'' .

It is difficult to understand why the corresponding exchange is so slow in the complexed ion pair $\text{Na}^+\text{C}, \text{Na}^-$ since this could also form a symmetric transition state with little solvent reorganization. If this were a major pathway, however, the exchange rate would be independent of both $[\text{Na}]_0$ and $[\text{C}]$. We must conclude, therefore, that the reaction of Na^+, Na^- with $\text{Na}^+\text{C}, \text{Na}^-$ provides the dominant mechanism for Na^+-Na^- exchange.

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Appendix

Reduction of the Three-Site Case to an Effective Two-Site System. The steady-state Bloch equations for three-site exchange are

$$-(\alpha_A + 1/\tau_A)G_A + \frac{G_B}{\tau_{BA}} + \frac{G_C}{\tau_{CA}} = i\gamma H_1 M_0 p_A \quad (\text{A-1})$$

$$-(\alpha_B + 1/\tau_B)G_B + \frac{G_A}{\tau_{AB}} + \frac{G_C}{\tau_{CB}} = i\gamma H_1 M_0 p_B \quad (\text{A-2})$$

$$-(\alpha_C + 1/\tau_C)G_C + \frac{G_A}{\tau_{AC}} + \frac{G_B}{\tau_{BC}} = i\gamma H_1 M_0 p_C \quad (\text{A-3})$$

in which G_j is the contribution to the complex magnetization from site j , $\alpha_j = 1/T_{2j} - i(\omega_j - \omega)$, and the other symbols have their usual meaning. As p_A approaches zero, the magnetization at site A becomes

$$G_A = \frac{G_B}{\tau_{BA}(\alpha_A + 1/\tau_A)} + \frac{G_C}{\tau_{CA}(\alpha_A + 1/\tau_A)} \quad (\text{A-4})$$

For small p_A the presence of site A has a significant effect on the NMR spectrum only if $1/\tau_A$ is very large (if A is an important intermediate for example), if $1/T_{2A}$ is very large (paramagnetic site for example), or if $\omega_j - \omega$ is very large (extreme chemical shift of species A). When, as in this work, site A is Na^+ in a simple ion pair at very low concentrations compared with complexed Na^+ , only the first of the above conditions can occur. This permits us to write

$$G_A = \frac{\tau_A}{\tau_{BA}} G_B + \frac{\tau_A}{\tau_{CA}} G_C \quad (\text{A-5})$$

(12) Khazaeli, S.; Popov, A. I.; Dye, J. L. *J. Phys. Chem.* **1982**, *86*, 4203, 5018.

(13) Khazaeli, S.; Popov, A. I.; Dye, J. L. *J. Phys. Chem.* **1983**, *87*, 1830.

Substitution into (A-2) and (A-3) gives

$$-[\alpha_B + 1/\tau_B']G_B + (1/\tau_C')G_C = i\gamma H_1 M_0 p_B \quad (\text{A-6})$$

$$-[\alpha_C + 1/\tau_C']G_C + (1/\tau_B')G_B = i\gamma H_1 M_0 p_C \quad (\text{A-7})$$

in which

$$1/\tau_B' = 1/\tau_B - \frac{\tau_A}{\tau_{AB}\tau_{BA}} = \frac{1}{\tau_{BC}} + \frac{\tau_A}{\tau_{AC}\tau_{BA}} \quad (\text{A-8})$$

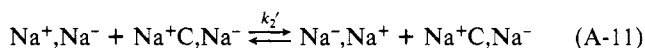
$$1/\tau_C' = 1/\tau_C - \frac{\tau_A}{\tau_{AC}\tau_{CA}} = \frac{1}{\tau_{CB}} + \frac{\tau_A}{\tau_{AB}\tau_{CA}} \quad (\text{A-9})$$

Equations A-6 and A-7 are identical in form to the two-site Bloch equations so that line shape analysis appropriate to the two-site case can be used. It may also be shown that

$$\tau_B'/\tau_C' = p_B/p_C \quad (\text{A-10})$$

which for the case considered in this paper ($p_B = p_C = 0.5$) gives $\tau_B' = \tau_C' = \tau$.

Derivation of the Exchange Rate for Mechanism I. Mechanism I consists of eq 7-9. Site C consists of Na^- ion paired to two different cations, Na^+ and Na^+C . Therefore, for a step such as



in which Na^- (site C) in the ion pair Na^+, Na^- exchanges with Na^+ (site A) in the same ion pair, we have

$$\frac{1}{\tau_{AC}} = 2k_2'[\text{Na}^+\text{C}, \text{Na}^-] \quad (\text{A-12})$$

and

$$\frac{1}{\tau_{CA}} = 2k_2'[\text{Na}^+\text{C}, \text{Na}^-] \left\{ \frac{[\text{Na}^+, \text{Na}^-]}{[\text{Na}^+, \text{Na}^-] + [\text{Na}^+\text{C}, \text{Na}^-]} \right\} \quad (\text{A-13})$$

The ratio given in braces is required because only this fraction of Na^- is present in the ion pair Na^+, Na^- , so that the mean lifetime in site C, distributed between Na^+, Na^- and $\text{Na}^+\text{C}, \text{Na}^-$, is much longer than the mean lifetime of the ion pair Na^+, Na^- .

Proceeding in this way, we obtain in addition to eq A-12 and A-13

$$\frac{1}{\tau_{AB}} = k_1[\text{C}] \quad (\text{A-14})$$

$$\frac{1}{\tau_{BA}} = k_{-1} \quad (\text{A-15})$$

$$\frac{1}{\tau_{BC}} = 2k_2''[\text{Na}^+, \text{Na}^-] = \frac{2k_2''[\text{Na}^+\text{C}, \text{Na}^-]}{K_1[\text{C}]} \quad (\text{A-16})$$

$$\frac{1}{\tau_{CB}} = \frac{2k_2''[\text{Na}^+\text{C}, \text{Na}^-]}{1 + K_1[\text{C}]} \quad (\text{A-17})$$

With eq A-9 this gives (with $k_1[\text{C}] \gg 2k_2''[\text{Na}^+\text{C}, \text{Na}^-]$)

$$\frac{1}{\tau} = \frac{2k_1[k_2' + k_2''][\text{C}][\text{Na}^+\text{C}, \text{Na}^-]}{[1 + K_1[\text{C}]]\{k_1[\text{C}] + 2k_2'[\text{Na}^+\text{C}, \text{Na}^-]\}} \quad (\text{A-18})$$

Since $K_1[\text{C}] = p_B/p_A \gg 1$, and $[\text{Na}^+\text{C}, \text{Na}^-] = [\text{Na}]_0/2$, we obtain

$$\frac{1}{\tau} = \frac{k_{-1}(k_2' + k_2'')[\text{Na}]_0}{k_1[\text{C}] + k_2'[\text{Na}]_0} \quad (\text{A-19})$$

Since $k_1[\text{C}] \gg k_2'[\text{Na}]_0$, this simplifies to

$$\frac{1}{\tau} = \frac{(k_2' + k_2'')[\text{Na}]_0}{K_1[\text{C}]} \quad (\text{A-20})$$

Equation A-8 gives the same result for $1/\tau$ to within the approximation $p_A \approx 0$.

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Relationship between Structure and Reactivity for Metal Clusters Formed in Ion-Molecule Reactions in Decacarbonyldirhenium

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Relative rate constants for ion-molecule reactions in $\text{Re}_2(\text{CO})_{10}$ are reported. Electron impact produced fragment ions react with the parent to form cluster ions containing three and four metal atoms. Subsequent sequential reactions lead to cluster ions containing as many as ten rhenium atoms. Rate constants for $\text{Re}_n(\text{CO})_m^+$ ions decrease with increasing m . A correlation is found between the average electron deficiency per metal atom and the rate constant. An electron deficiency is assigned by using the 18-electron rule and assuming closed polyhedral structures for most of the ions. The relative rate constants increase rapidly with increasing electron deficiency until the deficiency reaches two electrons per rhenium atom. The rate constants then slowly approach a constant value close to the collision-limited rate. This is consistent with the notion that the rate constants are determined primarily by the degree of coordinative unsaturation of the metal atoms in the cluster ion reactant. This satisfactory structure-reactivity relationship also substantiates the structural assumptions made about the cluster ions in assigning electron deficiencies.

Introduction

Recently we reported relative rate constants for gas-phase anionic clustering reactions in pentacarbonyl iron.¹ The relative rate constants were found to be related to the electron deficiencies of the reactant anions. $\text{Fe}_n(\text{CO})_m^-$ ions with large electron de-

ficiencies reacted rapidly with $\text{Fe}(\text{CO})_5$ to form larger clusters. Reactant anions with small electron deficiencies reacted slowly, if at all. Electron deficiencies were determined by assuming that each metal atom in a given cluster required 18 electrons to satisfy its valency. The total number of valence electrons in the cluster divided by the number of iron atoms is the average number of

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(1) Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67.