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Potassium-39 NMR Study of the Complexation Kinetics of K^+ Ion by 18-Crown-6 in Some Nonaqueous Solvents

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Abstract: The kinetics of complexation of K^+ ion with the crown ether 18-crown-6 was studied in five solvents or solvent mixtures by ^{39}K NMR line-shape analysis. In 1,3-dioxolane the cation exchange proceeds via the biomolecular exchange mechanism instead of the dissociative one that other workers found to be operative in aqueous solutions. The activation energy for this exchange strongly depends on the solvent; it is 9.2 kcal mol^{-1} in acetone and methanol, 13.8 kcal mol^{-1} in acetone–dioxane (80:20 v/v), and about 16.8 kcal mol^{-1} in dioxolane. The differences in activation entropies, which vary between -4 cal deg^{-1} mol^{-1} in acetone and $+15$ cal deg^{-1} mol^{-1} in dioxolane, compensate to a large extent the differences in activation energies so that, with the exception of aqueous solutions, the exchange rates at 25 °C vary by a factor of less than 50.

It is somewhat surprising to note that while there are abundant data in the literature on the stabilities of various macrocyclic complexes in a number of different media, kinetic studies of crown ether complexes with alkali ions have been quite sparse. It appears, for example, that there is no information available on the complexation kinetics of these ions in nonaqueous solvents with an otherwise very much studied polyether, 18-crown-6.

Shchori et al.[1,2] used sodium-23 NMR to study the kinetics of complexation of the Na^+ ion with dibenzo-18-crown-6 and its derivatives in dimethylformamide, dimethoxyethane, and methanol solutions. The authors found that the activation energy for the decomplexation reaction was only minimally influenced by the nature of the solvents. It should be noted, however, that the solvents they used have quite similar solvating abilities.

A recent ^{23}Na NMR study in our laboratory of the anion and solvent influence on the complexation of the sodium ion by 18-crown-6[3] has shown that the exchange of the sodium ion between the free (solvated) and the complexed sites in tetrahydrofuran solutions at 25 °C can be slow on the NMR time scale. Thus for $18C6{\cdot}Na^+$ system containing an excess of the sodium salt, in tetrahydrofuran and 1,3-dioxolane solutions, the exchange is slow when $NaBPh_4$ is used but not with other sodium salts such as the prechlorate or the iodide. Such slow exchange had not been seen previously for crown ether complexes by ^{23}Na NMR. It was of interest to us to explore the reasons for this slow exchange. We also wished to determine the extent to which the activation energy for the release of an alkali cation from 18C6 depends on the solvent.

Shporer and Luz[4] used potassium-39 NMR to study kinetics of complexation of the potassium ion by dibenzo-18-crown-6 in methanol. We selected the same NMR techniques for our studies with 18-crown-6 since the differences in ^1H and ^{13}C chemical shifts are too small to allow a quantitative kinetic study. The magnetic properties of the ^{39}K nucleus are certainly not ideal, particularly because of its very low sensitivity; however, it has a large range of relaxation rates that makes this study possible.

Experimental Section

1. NMR Measurements. Potassium-39 NMR measurements were carried out on a Bruker WH-180 spectrometer at a field of 42.27 kG and a frequency of 8.403 MHz. Each sample (except for 1,3-dioxolane solutions) contained 10–20 volume % of the deuterated solvent as an internal lock. A saturated solution of potassium nitrite in D_2O was used as the external standard. Chemical shift values are referred to an infinitely dilute aqueous solution of potassium salt and are corrected for the difference in the bulk diamagnetic susceptibility of the reference and the sample.

Line-width calibrations were made with 0.25 M solution of potassium iodide in a 3:1 (by volume) H_2O–D_2O mixture. The half-height line width ($\Delta\nu_{1/2}$) of the ^{39}K resonance line of this solution was 7.5 ± 0.3 Hz (as compared to the smallest one reported in the literature[5] for potassium salts at infinite dilution in H_2O, i.e., 5.7 ± 0.6 Hz ($T_2 = 56 \pm 6$ ms)). This indicates that the line-width contributions from field inhomogeneities range from 1 to 2 Hz at the most. This contribution is smaller than, or comparable to, the estimated precision of our measurements, which is about 2% for successive runs with the same or different samples.[6] The relaxation rates $1/T_2$ were calculated from the line widths ($1/T_2 = \pi\Delta\nu_{1/2}$) of the absorption spectra.

Samples were placed in 15- or 20-mm o.d. spinning NMR tubes. In general the salt concentration was 0.05–0.10 M depending on the solubilities of salts or complexes.

2. Reagents and Solvents. Macrocyclic polyether 18-crown-6 (18C6, Aldrich) was precipitated as the acetonitrile complex;[7] the crystals were isolated and kept under vacuum at room temperature for 24 h to drive off the acetonitrile; mp 36–37 °C (lit. mp 36.5–38.0 °C,[8] 39–40 °C[9]).

All solvents were purified by standard methods.[6] The water content of purified solvents was checked by Karl Fischer titration and was always found to be <100 ppm.

Potassium salts were of reagent grade quality. They were recrystallized and dried under vacuum at 110 °C for 24 h.

3. Data Handling. The kinetic parameters were calculated by fitting the rate data at various temperatures to appropriate equations by using a weighted nonlinear least-squares program KINFIT.[10]

Results

The kinetics of complexation of 18C6 with the K^+ ion were studied in five neat or mixed solvents by using ^{39}K NMR line-shape analysis. The five solvent systems were acetone, acetone–1,4-dioxane mixture (80:20 v/v), acetone–THF mixture (80:20 v/v), methanol, and 1,3-dioxolane.

The choice of solvents was primarily dictated by the desire to compare several media of approximately the same donor ability, as expressed by the Gutmann donicity scale.[11] In addition, methanol was selected because the only reported kinetic study by ^{39}K NMR was carried out in this solvent,[4] thus allowing a comparison of our results with the previously published data. The two solvent mixtures were used to compare the complexation reaction kinetics in neat solvents and in solvent mixtures.

1. Characterization of the Solvated and the Complexed Sites in the Absence of Chemical Exchange. In order to obtain the transverse relaxation rates $1/T_{2A}$ and $1/T_{2B}$ and the chemical shifts

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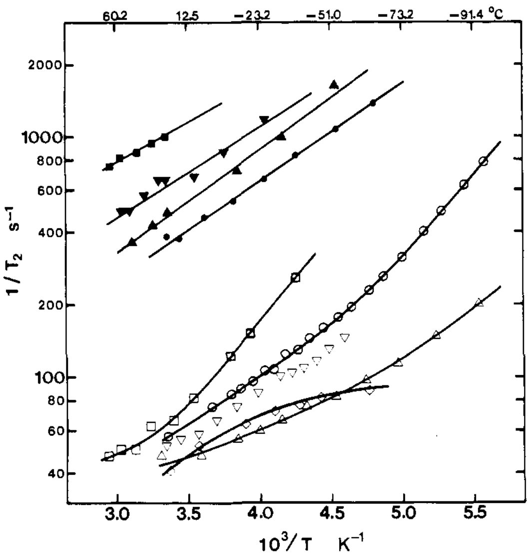

Figure 1. Semilog plots of ^{39}K transverse relaxation rates vs. reciprocal temperature for the solvated (open symbols) and the complexed (filled symbols) sites in various solvents: (□) dioxolane, (○) MeOH, (▽) acetone–dioxane, (◇) acetone–THF, (△) acetone.

Table I. Potassium-39 Chemical Shifts and Transverse Relaxation Rates for the Solvated (Site A) and the Complexed (Site B) K$^+$ Ions in Various Solvents at 25 °C

solvent	δ_A, ppm	δ_B, ppm	$\delta_A - \delta_B$, ppm	$\nu_A - \nu_B$, Hz	$1/T_{2A}$,[a] s^{-1}	$1/T_{2B}$, s^{-1}
acetone	−11.3	−3.2	8.1	68	80	487
acetone–1,4-dioxane (80:20 v/v)	−12.0	−3.5	8.5	71	52	657
acetone–THF (80:20 v/v)	−11.8	−2.3	9.5	80	50	487
1,3-dioxolane	−15.2	+0.4	15.6	131	80	1000
MeOH	−7.4	−2.5	4.9	41	65	386
DMF[b]	~−6	−3.8	~2.2	~18		~560
Me_2SO[b]	~+7	−0.6	~7.6	~64		
H_2O[b]	+0.5	−1.6	2.1	18		

[a] Extrapolated from the low-temperature $1/T_2$ (see text). [b] Data from J. S. Shih, Ph.D. Thesis, Michigan State University, 1978.

in the absence of exchange, δ_A and δ_B, where A and B indicate the solvated cation and the complexed cation sites, respectively, we prepared two solutions in each solvent that contained either the potassium salt alone or an equimolar amount of the salt and of 18C6. Since the K$^+$·18C6 complex is quite stable, log K_f = 6.05 in methanol,[12] it is clear that in the five solvent systems and at all temperatures studied, the concentration of free K$^+$ ion is negligible at equimolar concentrations of the ligand and the salt.

Semilog plots of the relaxation rates $1/T_{2A}$ and $1/T_{2B}$ vs. reciprocal absolute temperature are shown in Figure 1. In all solvents studied the plot is linear for the bound site but not for the solvated site. The corresponding chemical shifts and relaxation rates are given in Table I.

The quadrupolar relaxation rate for ^{39}K nucleus ($I = {}^3/_2$) in solution and in the absence of chemical exchange is given by the relationship[13]

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{1}{10}\left(1 + \frac{\beta^2}{3}\right)\left(\frac{eQ}{\hbar}\frac{\partial^2 V}{\partial z^2}\right)^2 \tau_c \qquad (1)$$

where β is the asymmetry parameter, Q is the quadrupole moment of the nucleus, $\partial^2 V/\partial z^2$ is the z component of the electrical field gradient at the nucleus produced by solvent fluctuations, and τ_c is the rotational correlation time for solvent molecules.

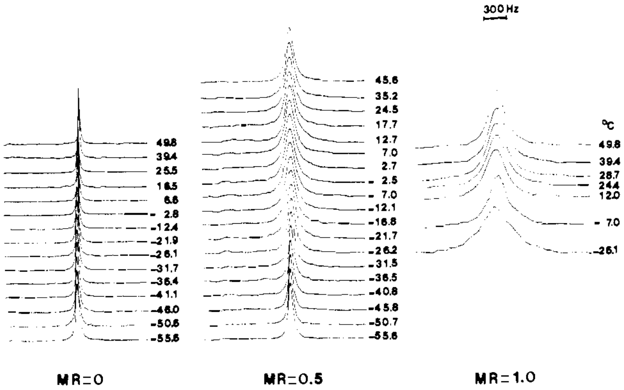

Figure 2. Potassium-39 NMR spectra of $KAsF_6$ + 18C6 solutions at various 18C6/K$^+$ mole ratios (MR) in a 80:20 (v/v) mixture of acetone and 1,4-dioxane at various temperatures.

For a simple activation process, τ_c may be expressed by

$$\tau_c = A \exp(-E_r/RT) \qquad (2)$$

where E_r is an activation energy for solvent reorientation.[14] This expression is more appropriate to our systems than the Debye equation

$$\tau_c = 4\pi\eta a^3/3kT \qquad (3)$$

(η = viscosity), which has been found to give too large values of the correlation times for solvated species[15] as well as for complexes.[16]

If the nuclear quadrupole coupling constant (NQCC) is independent of temperature, then the relaxation rate will vary exponentially with the temperature. As can be seen in Figure 1, in all solvents studied we observed such behavior in the case of the bound cationic site. In contrast, the semilog plots showed considerable curvature for the free cations. In the latter case large deviations from linearity have also been observed for the Na$^+$ ion in pyridine,[17] dimethylformamide,[1] and methanol[18] solutions.

The Debye expression predicts that $1/T_2$ is proportional to η/T. Deviations from this behavior have also been reported, e.g., for the Na$^+$ ion in tetrahydrofuran solutions.[19] In some cases the ^{23}Na line width increases with temperature instead of decreasing, e.g., for Na$^+$BPh$_4^-$ in 1,3-dioxolane solutions.[20] In all of the above cases, either the NQCC changes with temperature or τ_c does not behave as predicted by eq 2.

The two species capable of producing field gradients at the potassium nucleus are solvent dipoles and anions. Consequently, in low-polarity media such as 1,3-dioxolane, a change in the extent of ion pair formation with temperature could account for the observed nonlinear behavior of the plots. On the other hand, in methanol solutions, where K$^+$I$^-$ ion pairs are likely to be of the solvent-separated type,[21,22] the large increase of $1/T_2$ at low temperature may arise from an increase in the activation energy for solvent reorientation around the cation, because the solvent dimers tend to form a network of polymers.[23] We assumed that NQCC is independent of temperature and calculated from the slope of the relaxation curve that in methanol solutions E_r, the activation energy for solvent reorientation, increases from 1.7 kcal

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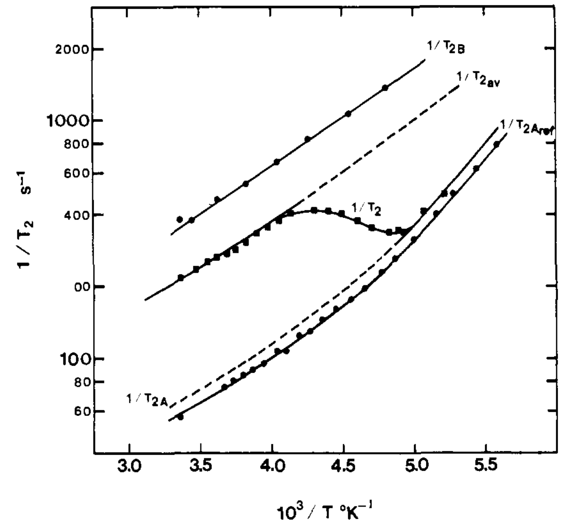

Figure 3. Semilog plots of $1/T_2$ vs. reciprocal temperatures for KI and 18C6 solutions in methanol at ligand/K$^+$ mole ratios of 0 ($1/T_{2\mathrm{Aref}}$), 0.5 ($1/T_2$), and 1.0 ($1/T_{2\mathrm{B}}$).

mol^{-1} at 10 °C to 3.2 kcal mol^{-1} at -90 °C. In less structured acetone solutions the corresponding E_r values are 1.2 and 2.0 kcal mol^{-1}, respectively.

Figure 3 shows a reversal of curvature of the plot in going from acetone to acetone-THF mixtures. At the present time we do not have an adequate explanation for this observation.

The relaxation rates of the bound site B are much larger than those of site A. This is mainly caused by the asymmetry of the electric field at the potassium nucleus due to the planar structure of the 18C6 crown ether.[24] The plots are linear and virtually parallel. The disappearance of curvature upon complexation of the K$^+$ ion by 18C6 points to a weak interaction between the complexed cation and the solvent. The relaxation rates for the solvated site decrease in the order dioxolane > methanol > acetone–dioxane > acetone for the solvated site whereas for the bound site it is dioxolane > acetone–dioxane > acetone > methanol.

It is seen in Table I that while the ^{39}K resonance of the free K$^+$ ion (site A) varies with the solvent over the range of about 22 ppm, the corresponding variation for the complexed cation is less than 5 ppm. These data indicate that the complexed cation is largely insulated from the solvent. Potassium ion fits nicely into the 18C6 cavity[24] so that only a small fraction of its surface is exposed to the solvent molecules. It should also be noted that in the solvents studied here, the difference in the chemical shifts of the two sites, $\delta_A - \delta_B$ (40–130 Hz) is quite small with respect to the relaxation rate of the complexed K$^+$ ion (400–1000 Hz at 25 °C).

2. Kinetic Studies. Kinetic parameters for the exchange of potassium ions between the solvated site and the K$^+$·18C6 complex were obtained from the temperature dependence of the ^{39}K transverse relaxation rates of solutions containing KAsF$_6$ (KI in methanol) and 18C6 with a 18C6/K$^+$ mole ratio of 0.5. Due to the large formation constants of the complex (see above), at equilibrium the concentration of the complex was essentially equal to that of the free cation.

Under our experimental conditions only one ^{39}K population-averaged resonance was observed throughout the temperature range covered. This is seen in the middle part of Figure 2 where typical spectra obtained in acetone–1,4-dioxane mixture are shown. Figure 3 shows a typical semilog plot of $1/T_2$ vs. $1/T$ for a methanol solution containing 0.20 M KI and 0.10 M 18C6. The observed pattern indicates a kinetic process in which K$^+$ ions exchange between the solvated and the complexed sites. In our cases ($\nu_A - \nu_B \ll 1/T_{2B}$) the rate data can be treated by the use of relationships that omit the chemical shift.[23] The standard method used was previously described by Shchori et al.[1]

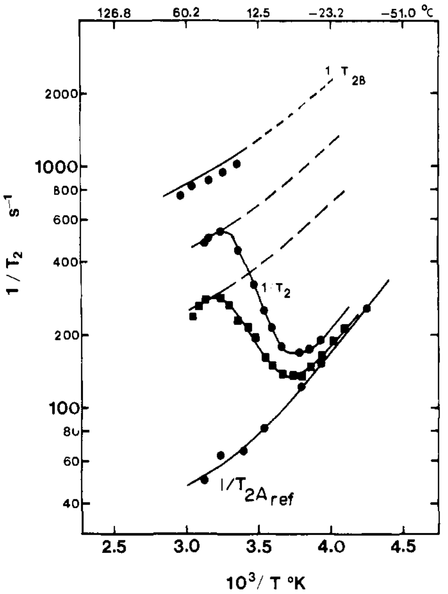

Figure 4. Semilog plots of $1/T_2$ vs. reciprocal temperature for KAsF$_6$ and 18C6 solution in 1,3-dioxolane: (top curve) K$^+$·18C6 complex (0.05 M); (middle full curves) (●) 18C6/K$^+$ = 0.5; (■) 18C6/K$^+$ = 0.25; (lower curve) KAsF$_6$ (0.1 M); (dashed curves) extropolation of $1/T_{2\mathrm{av}}$.

The reciprocal lifetime of the solvated species is given by

$$\frac{1}{\tau_A} = \frac{(1/T_{2B} - 1/T_2)(1/T_2 - 1/T_{2A})P_B}{1/T_{2\mathrm{av}} - 1/T_2} \tag{4}$$

where

$$1/T_{2\mathrm{av}} = P_A/T_{2A} + P_B/T_{2B} \tag{5}$$

and P_A and P_B are the respective populations of the ^{39}K nucleus at the two sites. The other symbols are explained in Figure 3.

The $1/T_{2A}$ values in the intermediate region were obtained by the extrapolation of the low-temperature values of $1/T_2$. We assumed that the temperature dependences of $1/T_{2A}$ and $1/T_{2\mathrm{Aref}}$ are parallel. In general, we were able to detect the signal of the complexed K$^+$ ion through a rather large temperature interval (Figure 3), which made it possible to check directly the validity of the above assumption.

The direct measurement of $1/T_{2B}$ increases the overall reliability of the results since the extrapolation of the high-temperature values of $1/T_2$ in order to obtain $1/T_2$ in the intermediate region is not required. Such extrapolation was necessary in the previous studies of Shchori et al.[1,2] and of Shporer and Luz[4] since these authors were unable to detect the signals for Na$^+$·DB18C6 and K$^+$·DB18C6, which are much broader than those of the corresponding 18C6 complexes.

3. Neat Solvents. Figures 3 and 4 show the observed relaxation rates in methanol and 1,3-dioxolane solutions. In going from acetone or methanol to 1,3-dioxolane, the active temperature range is shifted to higher temperatures by about 60 °C. In the latter solvent it is possible to observe the K$^+$ ion exchange between sites A and B at room temperature. Thus the slow exchange of the sodium ions between the solvated site and the Na$^+$·18C6 complex observed at 25 °C by Lin and Popov[3] in NaBPh$_4$ and 18C6 solutions in dioxolane and tetrahydrofuran is not an isolated case, and in these solvents the decomplexation rates of alkali ion crown complexes are considerably slowed down.

It is interesting to note that the complex K$^+$18C6·AsF$_6^-$ is much less soluble in THF (~0.01 M) and in dioxolane (~0.035 M) than the free salt or the ligand, which are ~0.2 M and >0.1 M, respectively, in both solvents.

The anion effect on the slow exchange observed earlier,[3] i.e., slow with NaBPh$_4$ and fast with NaI or NaClO$_4$, is probably due to the differences in the types of ion pairs formed in these solutions. It is believed that in tetrahydrofuran solutions NaBPh$_4$ forms

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Table II. Activation Parameters and Exchange Rates for $K^+\cdot 18C6$ Complexes in Various Solvents

	E_a,[a] kcal mol^{-1}	$\Delta H^\ddagger$,[b] kcal mol^{-1}	$\Delta S^\ddagger$,[b] cal K^{-1} mol^{-1}	$\Delta G^\ddagger$,[c] kcal mol^{-1} (298 K)	k,[d] M^{-1} s^{-1}	mechanism[e]
acetone	9.2 ± 0.5[f]	8.6 ± 0.5	-4 ± 2	9.8 ± 0.1[g]	$(4.1 \pm 0.9) \times 10^5$	I
acetone-1,4-dioxane	13.8 ± 0.5	13.2 ± 0.5	12 ± 2	9.6 ± 0.1	$(5.7 \pm 1.1) \times 10^5$	I
methanol	9.2 ± 0.7	8.6 ± 0.7	-3 ± 3	9.5 ± 0.2	$(6.8 \pm 2.7) \times 10^5$	I
			-8 ± 3	10.9 ± 0.2	$(6.8 \pm 2.7) \times 10^4$[h]	II
H_2O[i]	10.8	10.2	+3.1	9.3	3.7×10^6[h]	II
1,3-dioxolane	16.8 ± 0.3	16.2 ± 0.3	15 ± 1	11.70 ± 0.01	$(1.65 \pm 0.04) \times 10^4$	I
	15.5 ± 0.7	14.9 ± 0.7	11 ± 2	11.67 ± 0.03	$(1.74 \pm 0.09) \times 10^4$	I

[a] Arrhenius activation energy. [b] $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are the activation enthalpy and entropy, respectively. [c] $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. [d] $k = 1/(\tau_A[K^+\cdot 18C6])$. The values were either directly calculated or extrapolated from the values measured in the active temperature range. [e] See text for description of I and II. [f] Standard deviation estimated by KINFIT. [g] The standard deviation calculated by using the approximate equation $\sigma(\Delta G^\ddagger) \approx \sigma(\Delta H^\ddagger) - T\sigma(\Delta S^\ddagger)|$: Binsch, G.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* 1980, *19*, 411. [h] Units s^{-1}. [i] Reference 32.

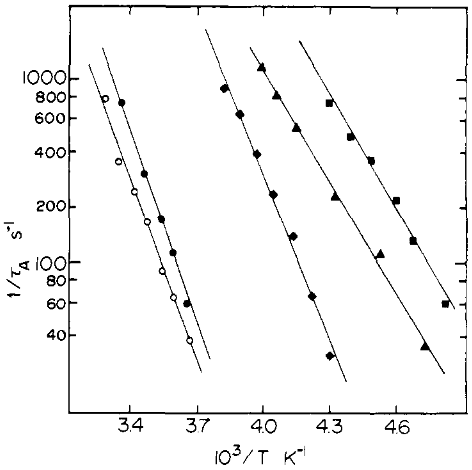

Figure 5. Plot of $1/\tau_A$ vs. $1/T$ in various solvents: (○) 1,3-dioxolane ($18C6/K^+ = 0.25$), (●) 1,3-dioxolane ($18C6/K^+ = 0.50$), (♦) acetone + 1,4-dioxane (80:20 (v/v)), (▲) acetone, (■) methanol.

solvent-separated ion pairs[26,27] whereas $NaClO_4$ and NaI tend to form contact ion pairs.[28] In the latter case the anions can compete with the ligand for the cation more effectively, which lowers the stability of the complex and increases the exchange rate. The particular effect of the BPh_4^- anion was recently confirmed by Sinta and Smid[29] who observed that the binding of an alkali tetraphenylborate to a polymeric crown ether network is much larger than that of the corresponding alkali picrate.

Figure 5 shows the Arrhenius plots of $1/\tau_A$ vs. $1/T$ in the five media. The plots are linear, and the activation energy values, obtained from the slopes in the usual manner, are given in Table II. The results of Liesegang et al.[30] are shown for comparison.

It is interesting to note the very strong solvent dependence of the activation energy, that which varies between 9.2 and 16.8 kcal mol^{-1}. The lower value, found in acetone and methanol, slightly exceeds the value of 8.4 kcal mol^{-1} reported earlier for the $Cs^+\cdot 18C6$ complex in pyridine solutions.[31] It compares well with the activation energies found for the release of the Cs^+ ion from DC18C6 (isomer A) in propylene carbonate[29] (8.5 kcal mol^{-1}) and of the Na^+ ion from DC18C6 (isomer B) in methanol.[2] The energy barrier to decomplexation is somewhat higher in water (10.8 kcal mol^{-1}) although this solvent exhibits a stronger donor character.[32]

Somewhat unexpectedly the value of E_a in dioxolane solution was found to be almost twice that found in acetone or methanol solutions. Two different samples with (ligand)/(K^+) mole ratios of 0.25 and 0.50 gave E_a values of 15.5 and 16.8 kcal mol^{-1}, respectively, which are in fair agreement considering the narrow temperature range accessible to study in this solvent. The activation energy in 1,3-dioxolane is comparable to the E_a values reported for some very stable cryptates such as $Li^+\cdot C211$ in various solvents, e.g., 16.1 kcal mol^{-1} in dimethyl sulfoxide. It also approaches the large E_a value of 18 ± 1 kcal mol^{-1} found for the decomplexation of t-$BuNH_3^+\cdot 18C6$ adduct in deuteriochloroform solutions.[34]

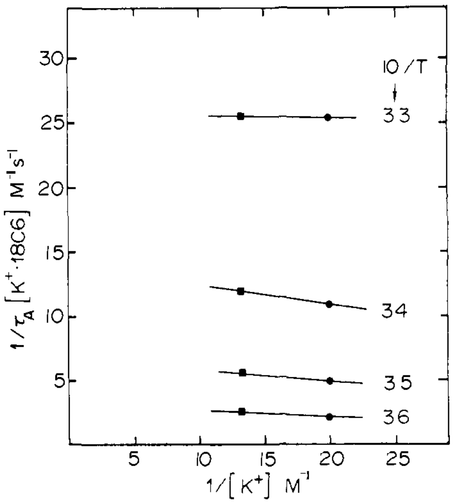

Figure 6. Plot of $1/(\tau_A[K^+\cdot 18C6])$ vs. $1/(K^+)$ in 1,3-dioxolane solutions at various temperatures.

The exchange of the K^+ ion between sites A and B may proceed via two mechanisms as proposed by Shchori et al.,[1,2] the bimolecular exchange process (I) and the dissociative mechanism (II).

$$\text{I} \qquad {}^*K^+ + K^+\cdot 18C6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^*K^+\cdot 18C6 + K^+ \qquad (6)$$

$$\text{II} \qquad K^+ + 18C6 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} K^+\cdot 18C6 \qquad (7)$$

Since these two mechanisms may contribute to the overall potassium ion exchange, the general expression for the reciprocal mean lifetime of the solvated species is

$$1/\tau_A = k_1[K^+\cdot 18C6] + k_{-2}[K^+\cdot 18C6]/[K^+] \qquad (8)$$

The contributions of mechanisms I and II may be determined by plotting $1/(\tau_A[K^+\cdot 18C6])$ vs. $1/[K^+]$. This was done for 1,3-dioxolane. The values of $1/\tau_A$ were measured for two samples with $18C6/K^+ = 0.25$ and 0.5, respectively (Figure 5). The ionic strength was kept constant at 0.1.[6] The plot of $1/(\tau_A[K^+\cdot 18C6])$ vs. $1/[K^+]$ is shown in Figure 6. The values of $1/(\tau_A[K^+\cdot 18C6])$ are constant within experimental error. The results indicate that

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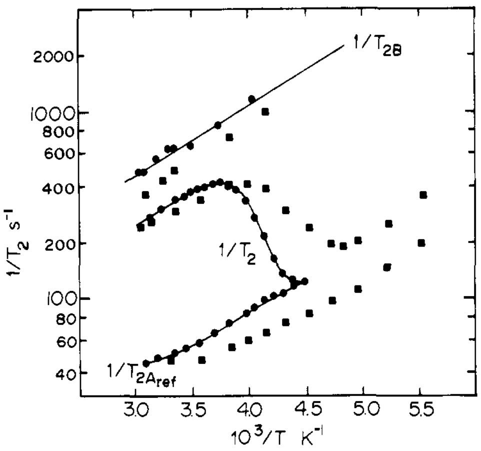

Figure 7. Semilog plot of $1/T_2$ vs. $1/T$ for (■) acetone and (●) acetone–dioxane solutions: (bottom) 0.10 M $KAsF_6$; (middle) 0.10 M $KAsF_6$ + 0.05 M 18C6; (top) 0.10 M $KAsF_6$ + 0.10 M 18C6.

the cation exchange proceeds via the bimolecular exchange (mechanism I).

The result was surprising since all previous studies for this type of complexes show that the cation exchange proceeds by the dissociative mechanism II.[35] In particular, Liesegang et al.[36] reported that for the $K^+\cdot$18C6 complex in water, where the decomplexation rates are much faster than in 1,3-dioxolane (Table II), mechanism II—coupled with a conformational rearrangement of the crown—best fits their ultrasonic relaxation data. Thus the solvent effect is so drastic that not only can it vary the activation energy but also can it change the mechanism; in the case of the system $Fl^-Na^+\cdot$dimethyl-DB18C6/THF-d_8, Wong et al.[37] postulated that the mechanism I is operative and calculated the exchange rate to be 3200 M^{-1} s^{-1} at 2 °C. Live and Chan[38] observed that the exchange rates are small in ethereal solvents and in $CDCl_3$.

We could not test the mechanism in methanol and acetone solutions in the same way as we did in dioxolane because in these solvents the T_{2A}/T_{2B} ratio is not very large (Figure 3). Hence for solutions with 18C6/K^+ mole ratio inferior to 0.5, the calculation of $1/\tau_A$ would be subject to a relatively large error. We can, however, deduce the mechanism from the following considerations. If we assume that in methanol the measured activation energy of 9.2 kcal mol^{-1} is that of the decomplexation step (mechanism II), the rate of release of the K^+ ion from the 18C6 complex may be calculated at 25 °C by extrapolating the low-temperature values of k_{-2}. Such extrapolation yields a value of k_{-2} of 6.8 × 10^4 s^{-1}, which, combined with the $K^+\cdot$18C6 formation constant of $10^{6.05}$,[10] yields $k_2 = 7.6 \times 10^{10}$ M^{-1} s^{-1} at 25 °C, which is about 1 order of magnitude larger than the limiting value for a diffusion-controlled reaction in methanol.[39,40] At least two reasons may be invoked for this discrepancy; firstly, it was noted by Liesegang et al.[40] that in such a case the k_{-2} and E_a values may not lend themselves to an extended extrapolation (-61 to 25 °C), i.e., E_a may vary with temperature; secondly (and more likely), mechanism I may contribute to the cation exchange, thus making the observed rate of decomplexation much larger than the rate calculated for mechanism II. The same reasoning applies to the acetone solutions.

4. Mixed Solvents. Semilog plots of $1/T_2$ vs. $1/T$ for the mixtures acetone–dioxane (80:20 v/v) and acetone–THF (80:20 v/v) are shown in Figures 7 and 8, respectively. The results obtained in neat acetone are reproduced in both figures for comparison.

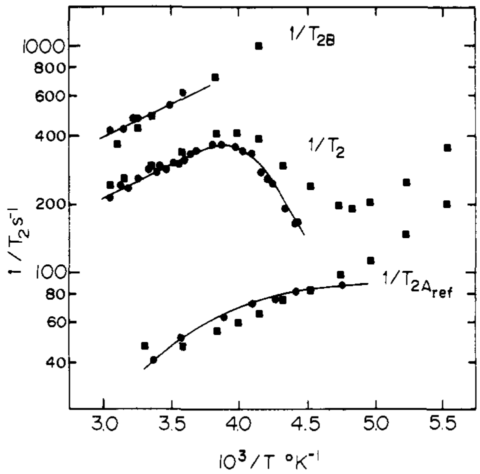

Figure 8. Semilog plots of $1/T_2$ vs. $1/T$ for (■) acetone and (●) acetone–THF solutions: (bottom) 0.10 M $KAsF_6$; (middle) 0.10 M $KAsF_6$ + 0.05 M 18C6; (top) 0.10 M $KAsF_6$ + 0.10 M 18C6.

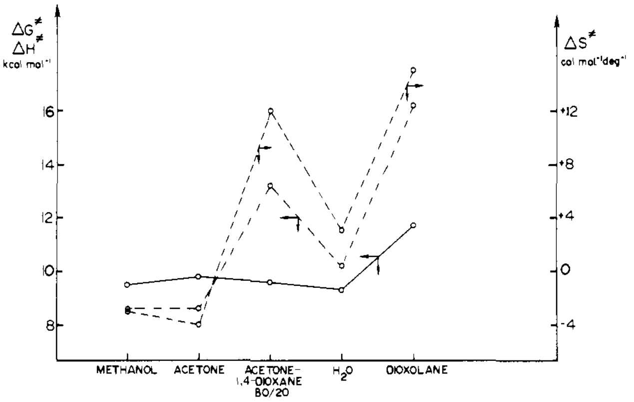

Figure 9. Variations of the $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ values for the decomplexation reaction in different media: (-·-) $\Delta H^{\ddagger}$, (—) $\Delta G^{\ddagger}$.

It is clear that the addition of an ethereal solvent to acetone shifts the kinetic process to higher temperatures and increases the activation energy. These effects are more pronounced with 1,4-dioxane than with tetrahydrofuran.

Below -20 °C the solubility of the $K^+\cdot$18C6 complex in the acetone–THF mixture is less than 0.05 M. However, the measurements could be performed on the unstable supersaturated solution during the short time available between the temperature stabilization and the formation of crystals. Below -48 °C, good quality spectra could not be obtained with this technique. Therefore, the low-temperature portion of the $1/T_2$ curve (Figure 8, middle full curve) and the $1/T_{2A}$ values, extrapolated from it, are missing, which precludes the calculation of the activation energy for this solvent system.

The dioxane-containing mixture is more amenable for a quantitative study since the $1/T_2$ values could be measured down to the minimum of the $1/T_2$ curve. The semilog plot of $1/\tau_A$ vs. $1/T$ shown in Figure 5 yields an activation energy of 13.8 kcal mol^{-1}. Thus in going from acetone to the acetone–dioxane mixture, in which the mole fraction of the latter is only 0.18, the activation energy increases by as much as 4.6 kcal mol^{-1}. These data confirm the results obtained in dioxolane solutions that ethereal solvents drastically increase the activation energy for the removal of the cation from the macrocyclic cavity.

The treatment of the exchange rates with the absolute rate theory of Eyring yields the activation parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ given in Table II. Mechanism I was assumed to be operative in all the solvents used in this study. Figure 9 shows the variation of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ with the solvent.

Discussion

Since the activation energy varies over a broad range with the solvent, it appears that it is not directly related to the energy

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required for a conformational rearrangement of the crown upon decomplexation. Table II shows that the large difference in $\Delta H^{\ddagger}$ between acetone and methanol solutions on one hand and the acetone–dioxane mixture on the other is nearly exactly compensated by the change in $\Delta S^{\ddagger}$. Such a compensating effect is not uncommon when a given reaction is studied in a series of solvents;[41] for example, it was observed in the case of $Li^+\cdot$C211 cryptates.[33]

In dioxolane the compensation is not quantitative although in this medium $\Delta S^{\ddagger}$ is larger and $\Delta G^{\ddagger}$ is larger by ~2 kcal mol^{-1} than in the other solvents.

We would like to suggest that the large $\Delta H^{\ddagger}$ values in dioxolane as well as in a acetone–dioxane mixture is indicative of a weak solvation of the K^+ ion in the transition state. In fact, Bhattacharyya et al.[43] have shown that the large alkali cations are almost not solvated by tetrahydrofuran. It would be expected that the same lack of solvation would be observed in 1,3-dioxolane.

The mechanism I, which we found applicable in our systems, is also favored on stereochemical grounds. The 18C6 molecule is symmetrical, and the probabilities of an access of the cation to the 18C6 binding sites from both "faces" of the crown are identical. Likewise, in the $K^+\cdot$18C6 complex, in contrast to Na^+18C6, the cation lies in the center of the crown ring.[44] The most likely transition state for mechanism I involves the symmetrical dicationic complex $K^+\cdot$18C6$\cdot K^+$.

The slow exchange between free solvated alkali cation and its 18C6 complex presents many interesting aspects. Further studies are needed in other solvent systems before its nature can be clearly elucidated. Such studies are being continued in our laboratories.

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Registry No. K, 7740-09-2; 18C6, 17455-13-9; ^{39}K, 14092-91-2; $K^+\cdot$18C6, 31270-13-0; THF, 109-99-9; 1,3-dioxolane, 646-06-0; acetone, 67-64-1; methanol, 67-56-1; 1,4-dioxane, 123-91-1.

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Spectroscopic, Electrochemical, and Photochemical Properties of Molybdenum(II) and Tungsten(II) Halide Clusters

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Abstract: The cluster ions $Mo_6Cl_{14}^{2-}$, $Mo_6Br_{14}^{2-}$, and $W_6Cl_{14}^{2-}$ are luminescent, with emission maxima (lifetimes, quantum yields) of 805 (180, 0.19), 825 (130, 0.23), and 880 nm (2 μs, 0.02), respectively, in acetonitrile at room temperature. Absorption spectra at low temperature reveal weak shoulders at low energy ($Mo_6Cl_{14}^{2-}$, 530 and 590 nm; $Mo_6Br_{14}^{2-}$, 600 nm; and $W_6Cl_{14}^{2-}$, 490 and 550 nm) that may be electronically closely related to the luminescences. Solid $(Bu_4N)_2Mo_6Cl_{14}$ is rigorously diamagnetic, and the paramagnetic $Mo_6Cl_{14}^-$ ion formed from it by one-electron oxidation gives an axial EPR spectrum ($g_\perp = 2.10$; $g_\parallel = 2.0$). All three ions undergo facile electrochemical oxidation, at potentials of 1.60, 1.38, and 1.14 V, respectively, vs. SCE in CH_3CN. Kinetics and rate constants are discussed for electron-transfer quenching of the luminescent excited state $Mo_6Cl_{14}^{2-*}$ by several electron acceptors, both in aqueous and nonaqueous solutions, and for the subsequent electron-transfer reactions.

The halides of molybdenum(II) were first described by Blomstrand in 1859.[1] Soon afterwards the first report of the analogous tungsten compounds appeared.[2] Although various reports of the chemistry of these compounds suggested that they were polynuclear, the first definite structural characterization was a crystallographic study of $[Mo_6Cl_8](OH)_4\cdot 14H_2O$.[3] The high overall symmetry of the staphylonuclear[4] cluster ion was established in 1950 by Vaughan in a crystal structure analysis of $(NH_4)_2Mo_6Cl_{14}\cdot H_2O$.[5] In idealized cubic symmetry, the $Mo_6Cl_{14}^{2-}$ ion consists of an octahedron of metal atoms surrounded by eight face-bridging and six axial halides. The existence of the M_6X_8 core has been demonstrated in a number of compounds: the dihalides M_6X_{12}, for example, are isomorphous, with the central M_6X_8 unit surrounded by four bridging and two terminal halides.[6]

Although substitution reactions are well documented for these cluster species, redox processes have previously been known to occur only with some difficulty and are often accompanied by major structural change. Our discovery that the clusters are intensely luminescent and undergo facile ground- and excited-state electron-transfer reactions[7] stimulated us to investigate more thoroughly the spectroscopic, electrochemical, and photochemical properties of $Mo_6Cl_{14}^{2-}$, $Mo_6Br_{14}^{2-}$, and $W_6Cl_{14}^{2-}$. The data presented here shed new light on the electronic structure of the clusters.

Experimental Section

Cluster Compounds. Molybdenum dichloride (Cerac, Inc.) was converted to $(H_3O)_2Mo_6Cl_{14}\cdot 6H_2O$ by the method of Sheldon.[8] This salt

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