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KINETIC STUDIES OF COMPLEXATION OF DIVALENT STRONTIUM, BARIUM,
LEAD AND MERCURY CATIONS BY AQUEOUS 15-CROWN-5 AND 18-CROWN-6

by

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limiting step in the complexation. Loss of coordinated water from the ions is proposed as the rate determining step.

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KINETIC STUDIES OF COMPLEXATION OF DIVALENT STRONTIUM, BARIUM, LEAD AND
MERCURY CATIONS BY AQUEOUS 15-CROWN-5 AND 18-CROWN-6.

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Neil Purdie,^{1c} and Edward M. Eyring.^{*1b} Contribution from the Department
of Chemistry, University of Utah, Salt Lake City, Utah 84112.

ABSTRACT

The rates of complexation-decomplexation of the 15-crown-5 [1,4,7,10,13-pentaoxacyclopentadecane] and 18-crown-6 [1,4,7,10,13,16-hexaoxacyclooctadecane] complexes of the aqueous cations Sr^{2+} , Ba^{2+} , Pb^{2+} and Hg^{2+} have been determined from ultrasonic absorption measurements covering the 15-205 MHz frequency range at 25°. As in the case of previously reported studies of complexation of monovalent cations by these crown ethers, the data have been fitted to a two-step mechanism. Diffusion has been ruled out as the rate limiting step in the complexation. Loss of the coordinated water from the ions is proposed as the rate determining step.

INTRODUCTION

Interest in the solution chemistry of the synthetic macrocyclic polyethers has increased greatly since their introduction by Pedersen,² stimulated by the many chemical and biological applications of these ligands as complexing and transport agents for metal ions.

In a previous kinetic investigation³ of the complexation equilibria between monovalent metal ions and the crown ethers Chock proposed a mechanistic scheme involving a ligand conformational rearrangement followed by the stepwise substitution of the coordinated solvent molecules by the ligand. Kinetic studies

in this laboratory⁴⁻⁶ of aqueous monovalent metal ion and ammonium ion complexation by 18-crown-6 and 15-crown-5 have confirmed the existence of at least one conformational rearrangement equilibrium for each of the ligands. Furthermore, one conformer strongly predominates in each such conformational equilibrium; the predominant form is involved in the metal ion complexation equilibrium; and complexation is not diffusion controlled.

The kinetics of the complexation equilibria involving these same crown ethers with some divalent metal ions is considered here. If loss of coordinated water is rate limiting then complexation rates should be slower for divalent ions compared to monovalent ions. In making our choice of divalent ions, two with inert gas configurations, Sr^{2+} and Ba^{2+} , and two ions with non-spherical coordinations, Pb^{2+} and Hg^{2+} , were selected. By analogy with the results for monovalent ions where faster complexation rates were observed for non-spherically coordinated Ag^+ and Tl^+ ions, the rates of complexation of Pb^{2+} and Hg^{2+} by the polyethers might be anticipated to be greater than those for Sr^{2+} and Ba^{2+} . If such were the case, we would have additional evidence for water loss as the rate limiting step in the mechanism.

EXPERIMENTAL SECTION

Ultrasonic absorption measurements were made at $25 \pm 0.1^\circ$ over an acoustic frequency range from 15 to 205 MHz, using a computer controlled laser acousto-optic technique.⁷ The argon ion laser was operated at the 514.5 nm green line and the piezoelectric acoustic transducer element was a gold plated, 5 MHz frequency, X-cut quartz crystal which was driven at odd harmonics over the frequency range.

Solutions were prepared using deionized redistilled water. The 15-crown-5 and 18-crown-6 (Parish Chemical Company, Provo, Utah) were purified as described previously.^{4,6} The inorganic ions were all analytical reagent grade. Strontium and barium ions were in the form of chloride salts and stock solutions were prepared by weight. The lead and mercury ions were introduced as perchlorates. These latter stock solutions were standardized either gravimetrically (PbSO_4)⁸ or titrimetrically ($\text{Hg}(\text{CNS})_2$).⁹

RESULTS

Total sound absorption data, expressed as $(\alpha/f^2)_T \text{ Np cm}^{-1} \text{ s}^2$ (see paragraph at end of text regarding supplementary material) were analyzed in terms of relaxational and nonrelaxational contributions to the ultrasonic absorptions. In all cases only one relaxational process was detected. The best fit was obtained using the following one-relaxation equation:

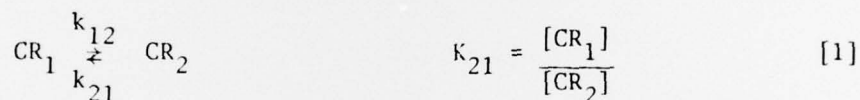
$$(\alpha/f^2)_T = A[1 + (f/f_R)^2]^{-1} + B$$

where A is the relaxation amplitude, f and f_R are respectively the experimental ultrasonic and relaxational frequencies and B is the solvent absorption, which was varied in the fitting process around the pure water value to take account of the structural changes in the solvent brought about by the added electrolyte. However, if the final best B value was in the range $21.7 \pm 0.5 \times 10^{-17} \text{ Np cm}^{-1} \text{ s}^2$, that of the pure water obtained on the present equipment, the central value $21.7 \times 10^{-17} \text{ Np cm}^{-1} \text{ s}^2$ was used in the fit as a fixed parameter.

Table I shows the parameters calculated at different concentrations of crowns and metal ions which give the best fit of the experimental data. The

resulting values of the relaxation frequencies, f_R , are in some cases below the lower limit of the experimental frequency range scanned with the present equipment. For several of these sample solutions complementary measurements were made¹⁰ on resonance ultrasonic spectrometers in the ~ 0.5 to ~ 5 MHz frequency range. Major discrepancies (factors as great as two) were noted in some of the amplitudes, but practically the same relaxation frequencies, f_R , were found from the composite ultrasonic data as were found originally in the laser acousto-optic measurements at Utah. Since none of the calculations or conclusions in this paper are based on the ultrasonic absorption amplitudes, uncertainties in their magnitudes are irrelevant to the present discussion.

Earlier studies in this laboratory of the complexation kinetics of monovalent metal ions by 15-crown-5 and 18-crown-6 were interpreted⁴⁻⁶ in terms of a two-step mechanism



previously suggested by Chock³ for the case of metal ion complexation by dibenzo-30-crown-10 in methanol. Although the relaxation time of the conformational step was not measured in Chock's study, a concentration independent relaxation frequency for pure crown in aqueous solutions has been reported for both 15-crown-5⁶ ($f_{R,I} = 22.9$ MHz) and 18-crown-6⁴ ($f_{R,I} = 101$ MHz). Accordingly it seems reasonable to expect that a two relaxation process should be observed when complexing electrolytes are present. The above reaction scheme

is mathematically described by the following secular determinant:

$$\begin{vmatrix} k_{12} + k_{21} - \lambda & -k_{21} \\ -k_{23} [M^{n+}] & k_{23} ([M^{n+}] + [CR_2]) + k_{32} - \lambda \end{vmatrix} = 0 \quad [3]$$

where $\lambda_i = 1/\tau_i$, and the extent of coupling is determined by the terms $-k_{21}$ and $-k_{23} [M^{n+}]$. In the case of complexation of monovalent cations by 15-crown-5, the analysis of the normal reactions and their amplitude factors showed that coupling does not exist since $k_{21} \ll k_{12}$ and the amplitude of the conformational step is negligibly small compared to that of the complexing step. In the 18-crown-6 case, τ_I^{-1} is sufficiently greater than τ_{II}^{-1} that coupling between the steps is insignificant and only one relaxation is observed when electrolytes are present. For the divalent ions, therefore an analogous two step mechanism is to be expected with the second step having the larger amplitude and thus giving rise to the detected relaxation. Consequently, the analysis of the kinetic data is made in terms of contributions from only this step, i.e.

$$\tau_{II}^{-1} = k_{23} ([\overline{CR_2}] + [\overline{M^{2+}}]) + k_{32} \quad [4]$$

The experimental equilibrium concentrations can be calculated from the equilibrium constants for the overall complexation K_T , reported by Izatt et al.¹¹ in the form:

$$K_T = \frac{[CR_2 M^{2+}]}{([CR_1] + [CR_2]) [M^{2+}]} \quad [5]$$

Taking into account the fact that $[CR_2] \gg [CR_1]$ since for both 15-crown-5 and 18-crown-6 $K_{21} \ll 1$, eq 4 can be arranged as

$$\tau_{II}^{-1} = k_{23} [(CR_1) + (CR_2) + (M^{2+}) + K_T^{-1}] \quad [6]$$

and k_{32} can subsequently be calculated from

$$k_{32} = \frac{k_{23}}{K_T} \quad [7]$$

In all cases the experimental kinetic data give an acceptable fit to eq 6. Table II shows the calculated k_{23} and k_{32} values obtained for the complexation of Sr^{2+} , Ba^{2+} , Pb^{2+} and Hg^{2+} by 15-crown-5 and 18-crown-6 following this procedure.

DISCUSSION

To add perspective to the kinetic results from the current work, data from previous studies⁴⁻⁶ on monovalent ions have been added to Fig. 1, which is a plot of the logarithm of k_{23} vs. the ratio of ion charge to ion size. There is an obvious separation between the ions with noble gas electronic configurations and the group of ions of the post transition elements. The observed linear dependence of $\log k_{23}$ for the first group is consistent with the decrease in charge density with increasing ionic size, and the increasing relative ease with which coordinated water is lost.

The observed rate constants k_{23} for complexation, Table II, may be compared with the rate constants¹² for substitution of water molecules from the inner coordination sphere of metal ions, k_o . All that is required is an estimate of the stability constant for outer sphere complex formation, K_o , in the relation

$$k_{23} = K_o k_{ex} \quad [8]$$

We estimate¹³ a value of $K_O = 0.32 \text{ M}^{-1}$. Thus for Ba^{2+} and 18-crown-6 $k_{23} = 1.3 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ would correspond to a $k_{\text{ex}} = 4 \times 10^8 \text{ sec}^{-1}$ that is smaller than the solvent substitution rate constant $k_O \sim 2 \times 10^9 \text{ sec}^{-1}$ reported by Winkler.¹² The other two cations, Sr^{2+} and Hg^{2+} , for which Winkler reports solvent substitution rate constants follow the same trend although in the case of mercury and 18-crown-6 $k_{\text{ex}} \approx 1.3 \times 10^9 \text{ sec}^{-1}$ is almost as large as $k_O \sim 2 \times 10^9 \text{ sec}^{-1}$.

Since we have not found a value of k_O for $\text{Pb}^{2+}(\text{aq})$ in the recent literature, we are not able to make the same sort of comparison of k_{ex} and k_O for this ion. However, it may prove useful to others to assume that our $k_{\text{ex}} = 1. \times 10^9 \text{ sec}^{-1}$ is only slightly smaller than the solvent exchange rate constant, k_O , for this ion.

There is no apparent dependence of the rates of complexation on the "hole" dimensions of the ligands. Variations in overall stability constants have already been related to parallel variations in k_{32} for either ligand.⁴⁻⁶ A dependence on ring dimensions is observed⁴⁻⁶ for decomplexation rates for all ions. The smaller ring separates faster than the larger ring, which is indicative of a greater conformational strain on the 15-crown-5 when it complexes.

Complexation rates for the transition and post transition metal ions differ in two ways from the rates for the noble gas configuration ions. They are all larger in magnitude (Fig. 1) and except for Pb^{2+} they show a distinct ligand dependence. A possible interpretation of the increased rate is that in the progressive substitution process fewer solvent molecules are lost. Also if the loss of coordinated water molecules other than the first is rate limiting, the rate of complexation could be enhanced by directional influences through the hybridization network of these ions. Silver(I) and mercury(II)

ions demonstrate the greatest dependence of k_{23} on the ligand. These ions commonly hybridize in sp geometry. A trans-directing influence, i.e. covalent bonding, of the coordinated ligand might enhance the rate of second substitution.¹⁴ At the same time the ligand would undergo considerable conformational strain to accommodate itself to the linear geometry of the metal. Again the strain would be greater for the smaller and inherently more rigid 15-crown-5 polyether thus accounting for the slower complexation rate with this ligand.

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SUPPLEMENTARY MATERIAL AVAILABLE

Raw ultrasonic absorption data (8 pages). Ordering information is given on any current masthead page.

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Table Ia. RELAXATION PARAMETERS FROM COMPUTER ANALYSIS FOR COMPLEXATION
BY 15-CROWN-5.^a

STRONTIUM				
$[\text{SrCl}_2]_0, \text{F}^b$	$[\text{15-Crown-5}]_0, \text{M}$	$f_{\text{R, II}}, \text{MHz}$	$10^{17} A, -1 \text{ sec}^2$ Np cm	10^{18}RMS^c
1.00	0.0877	9.95	157.9	1.0
1.51	0.0877	14.09	82.37	1.3
1.82	0.0797	18.33	48.89	1.0
BARIUM				
$[\text{BaCl}_2]_0, \text{F}$	$[\text{15-Crown-5}]_0, \text{M}$	$f_{\text{R, II}}, \text{MHz}$	$10^{17} A, -1 \text{ sec}^2$ Np cm	10^{18}RMS
0.756	0.0640	12.33	144.4	1.9
0.886	0.0864	14.14	146.8	1.8
1.01	0.0860	16.67	99.4	2.0
LEAD(II)				
$[\text{Pb}(\text{ClO}_4)_2]_0, \text{F}$	$[\text{15-Crown-5}]_0, \text{M}$	$f_{\text{R, II}}, \text{MHz}$	$10^{17} A, -1 \text{ sec}^2$ Np cm	10^{18}RMS
0.413	0.0783	19.72	69.17	1.2
0.516	0.130	20.80	83.87	1.8
0.688	0.0877	31.19	32.92	0.9
MERCURY(II)				
$[\text{Hg}(\text{ClO}_4)_2]_0, \text{F}$	$[\text{15-Crown-5}]_0, \text{M}$	$f_{\text{R, II}}, \text{MHz}$	$10^{17} A, -1 \text{ sec}^2$ Np cm	10^{18}RMS
0.590	0.114	14.97	759.3	2.3
0.871	0.111	18.91	572.1	2.3
1.15	0.107	26.20	287.1	1.9

^aAll symbols as defined in the text.

^bThe subscript zero on concentration denotes total concentrations.

^cRoot mean square deviation.

Table 1b. RELAXATION PARAMETERS FROM COMPUTER ANALYSIS FOR COMPLEXATION
BY 18-CROWN-6.*

STRONTIUM				
<u>[SrCl₂]₀, F</u>	<u>[18-Crown-6]₀, M</u>	<u>f_{R, II}, MHz</u>	<u>10¹⁷ A, -1 Np cm⁻¹ sec²</u>	<u>10¹⁸ RMS</u>
1.00	0.100	10.82	89.00	2.1
1.40	0.100	17.12	64.70	1.4
1.89	0.0920	20.97	46.25	1.1
BARIUM				
<u>[BaCl₂]₀, F</u>	<u>[18-Crown-6]₀, M</u>	<u>f_{R, II}, MHz</u>	<u>10¹⁷ A, -1 Np cm⁻¹ sec²</u>	<u>10¹⁸ RMS</u>
1.00	0.100	19.19	39.48	1.7
1.30	0.100	24.76 ^a	25.14	1.2
1.50	0.100	28.10 ^b	21.99	1.1
LEAD(II)				
<u>[Pb(ClO₄)₂]₀, F</u>	<u>[18-Crown-6]₀, M</u>	<u>f_{R, II}, MHz</u>	<u>10¹⁷ A, -1 Np cm⁻¹ sec²</u>	<u>10¹⁸ RMS</u>
0.242	0.0134	11.50 ^c	45.94	0.9
0.323	0.0179	16.37 ^c	30.92	0.5
0.430	0.0238	21.69 ^d	23.43	0.5
MERCURY(II)				
<u>[Hg(ClO₄)₂]₀, F</u>	<u>[18-Crown-6]₀, M</u>	<u>f_{R, II}, MHz</u>	<u>10¹⁷ A, -1 Np cm⁻¹ sec²</u>	<u>10¹⁸ RMS</u>
0.354	0.0400	21.80	71.28	1.0
0.472	0.0450	28.51	58.39	1.1
0.590	0.0500	32.55	55.76	1.2

* A background of ^a23.0 x 10⁻¹⁷; ^b22.7 x 10⁻¹⁷; ^c20.6 x 10⁻¹⁷; ^d20.2 x 10⁻¹⁷

Np cm⁻¹ sec² give the best fit to the experimental data

Table 11. RATE CONSTANTS FOR COMPLEXATION BY 15-CROWN-5 AND 18-CROWN-6 IN AQUEOUS SOLUTION AT 25° CALCULATED FROM ULTRASONIC ABSORPTION DATA.

Cation	15-Crown-5			18-Crown-6		
	$k_{23}, M^{-1} \text{sec}^{-1}$	k_{32}, sec^{-1}	K_T, M^{-1}	$k_{23}, M^{-1} \text{sec}^{-1}$	k_{32}, sec^{-1}	K_T, M^{-1}
Sr^{2+}	6.5×10^7	7.3×10^5	89.1	7.7×10^7	1.5×10^5	5.25×10^2
Ba^{2+}	1.1×10^8	2.1×10^6	51.3	1.3×10^8	1.7×10^4	7.41×10^3
Pb^{2+}	3.2×10^8	4.6×10^6	70.8	3.3×10^8	1.8×10^4	1.86×10^4
Hg^{2+}	1.6×10^8	3.3×10^6	47.9	4.0×10^8	1.5×10^6	2.63×10^2

^a Izatt et al., reference 11 of text.

Figure Caption.

Fig. 1 Plot of the logarithm of the rate constant for complexation, k_{23} , versus the ratio of ionic charge to ionic radius (arbitrary units) for complexation by 18-crown-6, $\circ$, and by 15-crown-5, $\bullet$. The straight diagonal line is a least squares fit of the alkali and alkaline earth metal data.

