Inorganica Chimica Acta, 64 (1982) L263–L265

Kinetics of Complexation of Dibenzo-18-Crown-6 with Strontium Ion in Methanol at –15 °C Studied by Stopped Flow Technique

B. G. COX

The Chemistry Department, University of Stirling, Stirling FK9 4LA, U.K.

P. FIRMAN and H. SCHNEIDER

Max-Planck-Institut für biophysikalische Chemie, D-3400 Göttingen, F.R.G.

Received January 9, 1982

Introduction

The mechanism of complexation of crown ethers with metal ions has been a subject of considerable interest during the past few years, because of their suitability as models for biochemical processes. Previous kinetic investigations of the complexation equilibria of monovalent and divalent metal ions with crown ethers in various solvents have been carried out using T-jump [1], ultrasonic absorption [2, 3] or NMR [4–6] methods, as the rates are too fast to be followed by conventional stopped-flow techniques. However, by analogy with cryptate complexes, for which formation rates in methanol of complexes involving alkaline earth cations are several orders of magnitude slower than those of the alkali metal cations, it was expected that rates of complexation of divalent cations with the less flexible dibenzo-18-crown-6 (DB18C6) in methanol might be slow enough at low temperatures to be followed by stopped-flow experiments. For this purpose, the system Sr^{2+} and DB18C6 was selected since the formation of this complex displays the most significant spectral change in the ultraviolet region [7].

Experimental

Stopped-flow measurements were carried out with spectrophotometric detection (267–270 nm) at –15 (±0.1) °C. For the formation rate measurements, an excess of Sr^{2+} ($(0.5–3.0) \times 10^{-3}$ *M* $Sr(NO_3)_2$) was mixed with DB18C6 solutions ($(0.1–0.3) \times 10^{-3}$ *M*). The ionic strength was kept constant at I = 0.05 *M* by the addition of $LiClO_4$ salt. For the decomplexation process, mixtures of DB18C6 and Sr^{2+} ([DB18C6] < [Sr^{2+}], $(0.1–0.3) \times 10^{-3}$ *M* DB18C6 and $(0.3–0.5) \times 10^{-3}$ *M* Sr^{2+}) were mixed with a large excess of scavenger solutions of cryptand (2,2,2) ($(1.4–10) \times 10^{-3}$ *M*). All reactions were first order and the data were treated by standard methods. DB18C6 was obtained from Fluka, $LiClO_4$ from Alfa, $Sr(NO_3)_2$ and methanol ($H_2O < 0.01\%$) from Merck.

Results and Discussion

Previous studies of the complexation kinetics of monovalent and divalent metal ions by various crown ethers [1–6] were interpreted in terms of a two step mechanism suggested by Chock [1] for the complexation of univalent metal ions by dibenzo-30-crown-10 in methanol at 25 °C. In eqns. (1) and (2), CR_1 and CR_2 refer to two different conformations of the crown ether.

$$\mathrm{CR_1} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{CR_2} \qquad (1)$$

$$\mathrm{CR_2} + \mathrm{M^{n+}} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{M(CR_2)^{n+}} \qquad (2)$$

Although Chock was unable to measure the kinetics of the fast conformational pre-equilibrium because of the limits of his apparatus, concentration independent relaxation frequencies for 18-crown-6 [4] and 15-crown-5 [8] solutions in the absence of metal ions have been observed using ultrasonic studies. However, more recent publications of 18-crown-6 complexation with both mono- and divalent cations in water have reported that $k_{12} \gg k_{21}$ (*i.e.* $[CR_1] \ll [CR_2]$), that coupling between steps (1) and (2) is insignificant, and that only one relaxation is observed when electrolytes are present [2, 3]. Since the pre-equilibrium (1) is too fast to be measured in our apparatus, the observed kinetics will be of the form shown in eqns. (3) and (4), where

$$\frac{-d\{[\mathrm{Sr(CR_2)^{2+}}]_\infty - [\mathrm{Sr(CR_2)^{2+}}]\}}{dt} = k_e\{[\mathrm{Sr(CR_2)^{2+}}]_\infty - [\mathrm{Sr(CR_2)^{2+}}]\} \qquad (3)$$

$$\text{with } k_e = k_{32} + \frac{k_{23}K_{12}}{1 + K_{12}}[\mathrm{Sr^{2+}}] \qquad (4)$$

$K_{12} = k_{12}/k_{21}$ is the equilibrium constant for (1). Furthermore, by taking into account that $K_{12} \gg 1$ ($[CR_2] \gg [CR_1]$), eqn. (4) reduces to (5) and the data can be analysed in terms of the single complexation step (6), where CR represents the total amount of the crown ether present.

$$k_e = k_{32} + k_{23}\,[\mathrm{Sr^{2+}}] \qquad (5)$$

0020-1693/82/0000-0000/$02.75

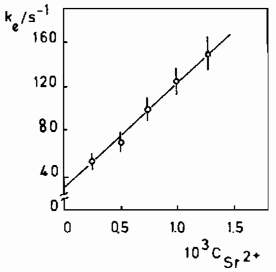

Fig. 1. Plot of k_e *vs.* concentration of Sr^{2+}.

$$CR + Sr^{2+} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} Sr(CR)^{2+} \tag{6}$$

The fit of the kinetic data according to equation (5) yields an excellent straight line (Fig. 1) and the plot gives values of 9.6 (±0.5) × 10^4 M^{-1} s^{-1} and (27 (±3) s^{-1} for k_{23} and k_{32}.

The decomplexation rate was measured by mixing the crown ether complex with a large excess of cryptand (2,2,2).

$$SR(CR)^{2+} \underset{k_{23}}{\overset{k_{32}}{\rightleftharpoons}} CR + Sr^{2+} \tag{7}$$

$$Sr^{2+} + (2,2,2) \xrightarrow{k} Sr(2,2,2)^{2+} \tag{8}$$

It follows that if $d[Sr^{2+}]/dt = 0$, we may write for the observed rate constant, k_e,

$$k_e = \frac{k_{32}k[2,2,2]}{k_{23}[CR] + k[2,2,2]} \tag{9}$$

which can be rewritten as

$$\frac{1}{k_e} = \frac{1}{k_{32}} + \frac{K_{23}[CR]}{k[2,2,2]} \tag{10}$$

where

$$K_{23} = k_{23}/k_{32} = [Sr(CR)^{2+}]/[CR][SR^{2+}] \tag{11}$$

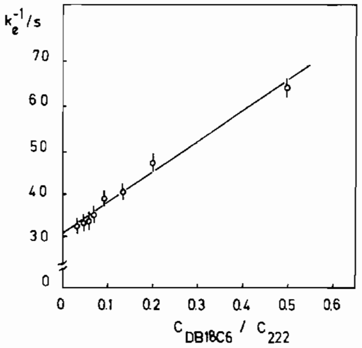

Fig. 2. Plot of $1/k_e$ according to eqn. (10).

The observed rate constants were then plotted according to eqn. (10) and show the dependence predicted by the proposed mechanism. [CR] and [2,2,2] are the averages of the concentrations at the beginning and at the end of the reaction. From the plot of eqn. (10) shown in Fig. 2 we have estimated the values of k_{32} = 31 (±3) s^{-1}, which is in excellent agreement with the value of k_{32} = 27 (±3) s^{-1} from the plot of eqn. (5), and a value of k = 5.4 (±1.0) × 10^4 M^{-1} s^{-1} for the formation rate of the cryptate $Sr(2,2,2)^{2+}$. The latter value was obtained from the slope in Fig. 2, together with the measured value, K_{23} = 3.6 × 10^3 M^{-1}, for the formation of $Sr(CR)^{2+}$ reported above.

The results of this study are compared in Table I with those obtained earlier for some related reactions of other macrocyclic ligands. Results for M^{2+} systems in methanol are very limited, but allowing for the temperature difference, the formation rates for the two ligands studied here are about one to two orders of magnitude faster than those of the peptide antamanide [9]. In the case of Ca^{2+}, part of the reason for the slower rate is the greater solvation energy of Ca^{2+} compared with Sr^{2+}, but undoubtedly larger conformational changes are required for the formation of the antamanide complexes.

TABLE I. Rates and Stability Constants of some Complexes with Macrocyclic and Bicyclic Ligands.

Complex	Solvent	Temp.	k_f/M^{-1} s^{-1}	k_d/s^{-1}	K_s/M^{-1}	Ref.
Sr^{2+}–DB18C6	MeOH	−15 °C	(9.6 ± 0.5) 10^4	(2.7 ± 0.3) 10^1	3.6 × 10^3	(this work)
Sr^{2+} (2,2,2)	MeOH	−15 °C	(5.4 ± 1.0) 10^4	6.8 × 10^{-9} [a]	7.9 × 10^{12} [b]	(this work)
Na_2^+–Antamanide	MeOH	25 °C	1.1 × 10^5	2.1 × 10^2	5 × 10^2	[9]
Ca^{2+}–Antamanide	MeOH	25 °C	4.9 × 10^3	1.9 × 10^2	2.5 × 10^1	[9]
Sr^{2+}–15C5	H_2O	25 °C	6.5 × 10^7	7.3 × 10^5	8.91 × 10^1	[8]
Sr^{3+}–18C6	H_2O	25 °C	7.7 × 10^7	1.5 × 10^5	5.25 × 10^2	[8]

[a] Value calculated from the K_s value in 95/5 wt.% MeOH/H_2O and k_f in MeOH [10]. [b] Value calculated from the results in 95/5 wt.% MeOH/H_2O [10].

The formation rates of the dibenzo-18-crown-6 and the (2,2,2) complexes with Sr^{2+} are very similar, despite the fact that steric effects are expected to be different for the mono- and bicyclic ligands. Both are significantly smaller than the corresponding rates of the Sr^{2+} complexes with 15-crown-5 and 18-crown-6 in water [3]. Since the cavity radius of dibenzo-18-crown-6 (1.26–1.38 Å) [11] is similar to that of (2,2,2) (1.4 Å) [13], and both are larger than the ionic radii of Sr^{2+} (1.13 Å) [13], the rate limiting process is expected to be the desolvation of Sr^{2+}. A similar conclusion may be drawn from the results of Burgermeister *et al.* [9] for antamanide complexes with Na^+ and Ca^{2+} in methanol which show a dependence of the formation rates upon the solvation energies of the ions. This dependence fails for the dissociation rates.

Perhaps the most striking influence of ligand structure on the kinetic behaviour recorded in Table I may be seen in the dissociation rates. Thus the various ligands all show relatively rapid formation rates, which do not correlate in any simple way with ligand structure. However, the more flexible crown ethers and antamanide also show quite fast dissociation rates, *i.e.* overall exchange rates are rapid, while the dissociation rate of $Sr(2,2,2)^{2+}$ is some 10^8 times slower than that of any of the other ligands. The stability constant for the complex is correspondingly high. Thus, although the particular bicyclic structure of (2,2,2) does not appear to influence the formation rates strongly, it has a dramatic effect on the dissociation rates and stability constants.

References

1 P. B. Chock, *Proc. Natl. Acad. Sci., U.S.A., 69,* 1939 (1972).
2 G. W. Liesegang, M. M. Farrow, F. A. Fazquez, N. Purdie and E. M. Eyring, *J. Am. Chem. Soc., 99,* 3240 (1977).
3 L. J. Rodriquez, G. W. Liesegang, M. M. Farrow, N. Puride and E. M. Eyring, *J. Phys. Chem., 82,* 647 (1978).
4 E. Shchori, J. Jagur-Grodzinski, Z. Luz and M. Shporer, *J. Am. Chem. Soc., 93,* 7133 (1971).
5 E. Shchori, J. Jagur-Grodzinski and M. Shporer, *J. Am. Chem. Soc., 95,* 3842 (1973).
6 M. Shporer and Z. Luz, *J. Am. Chem. Soc., 97,* 89 (1975).
7 C. J. Pedersen, *J. Am. Chem. Soc., 89,* 7017 (1967).
8 G. W. Liesegang, M. M. Farrow, N. Purdie and E. M. Eyring, *J. Am. Chem. Soc., 98,* 6905 (1976).
9 W. Burgermeister, T. Wieland and R. Winkler, *Eur. J. Biochem., 44,* 305 (1974).
10 J. D. Lamb, R. M. Izatt, J. J. Christensen and D. J. Eatough, in 'Coordination Chemistry of Macrocyclic Compounds', ed., G. A. Melson, Plenum Press, New York, 1979.
11 N. K. Dalley, in 'Synthetic Multidentate Macrocyclic Compounds', ed. R. M. Izatt, J. J. Christensen, Academic Press, New York, 1978.
12 J. M. Lehn, *Struct. Bonding (Berlin), 16,* 1 (1973).
13 L. Pauling, 'The Nature of the Chemical Bond', 3rd ed., p. 260, Cornell Univ. Press, Ithaca, New York, 1960.