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Molecular dynamics of macrocycle–metal ion complexes involving heteronuclear binding atoms

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Abstract - Combination of ultrasonic absorption relaxation spectra with infrared absorption spectra yields a clearer picture of the mechanism of complexation of metal ions by macrocycles in nonaqueous solutions. The Eigen-Winkler multistep reaction mechanism has consistently provided a suitable fit of the ultrasonic absorption data for systems such as monovalent sodium cation reacting with 18-crown-6 in acetonitrile. A macrocycle such as Kryptofix 22 having two nitrogen atoms in the ring experiences an exo-exo ⇄ exo-endo ⇄ endo-endo change in conformation readily detected by ultrasonic techniques. Differences in complexation-decomplexation mechanisms deduced from ultrasonic and NMR data can be rationalized in terms of the limitations of the experimental techniques.

INTRODUCTION

Ultrasonic absorption data in the frequency range between 0.5 and 500 MHz can be collected by a judicious combination of ultrasonic resonators, laser Debye-Sears diffraction experiments and ultrasonic pulse methods (ref. 1). Early examples of the use of ultrasonic methods to study rates and mechanisms of reactions of macrocycles include a classic study of sodium cation complexation by valinomycin in methanol (ref. 2) and several papers describing monovalent and divalent cations undergoing complexation by 18-crown-6 and 15-crown-5 in aqueous solutions (ref. 3). In recent years we have shifted our attention to kinetic studies of macrocycles reacting with cations in aprotic solvents (ref. 4). To some extent this new interest has been driven by practical considerations such as the exploration of reaction rates in lithium battery electrolytes (ref. 5).

The Eigen-Winkler multistep reaction mechanism (ref. 6) may be written as

$$M^+ + C \underset{k_{-o}}{\overset{k_o}{\rightleftarrows}} M^+...C \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MC^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} (MC)^+ \qquad (1)$$

Here M^+ denotes the metal ion, C the macrocycle, $M^+...C$ a solvent separated pair, MC^+ a contact pair of solutes, and $(MC)^+$ the metal ion imbedded in the cavity of the macrocycle. Scheme 1 is necessarily a considerable oversimplification since each of the species can exist in more than one configuration (ref. 6). In the first step (on the left) an outer-sphere complex forms requiring some change in the conformation of the ligand C and partial desolvation of the cation. The third step (proceeding from left to right) can be rate limiting either by desolvation (as in water) or by ligand rearrangement. The relatively high permittivity of aqueous solutions favors high concentrations of the free metal ions. The competition of solvent water molecules with counteranions and macrocyclic ligands for positions in the first coordination sphere of the metal ion is tilted heavily in favor of the solvent water. The familiar generalization (ref. 7) for aqueous solutions that the rate limiting step in metal-ligand complex formation is the loss of a solvent water molecule from the first coordination sphere of the metal ion arises from this unequal competition between solvent, counteranion, and ligand suitors.

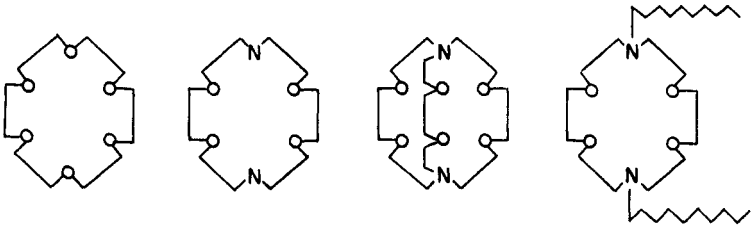
In every aprotic solution of metal ions and macrocycles that we have studied so far with ultrasonics the Eigen-Winkler mechanism accounts satisfactorily for the kinetic data. However, the competition between solvent, anion and ligand is more nearly equal. For instance, in dimethylformamide 18-crown-6 complexes the divalent barium cation faster than it does the monovalent potassium cation (ref. 8). Just the opposite is the case in aqueous solution where the higher charge density of the barium cation holds the first coordination sphere solvent water molecules more securely than the monovalent potassium ion can (ref. 3). In the case of the complexation of monovalent silver cation by 18-crown-6 in dimethylformamide it has been shown that the rate limiting step of complexation is a ligand rearrangement around the cation since 18-crown-6 reacts more rapidly with the silver cation than the more rigid dibenzo-18-crown-6 ligand does (ref. 9). In aprotic solvents the counteranion competes effectively with solvent and macrocyclic ligands for first coordination sphere metal ion sites and one sees very different relaxation frequencies and ultrasonic absorption maxima when, for example, $AgNO_3$ reacts with 18-crown-6 in dimethylformamide instead of $AgClO_4$ (ref. 9). If the aprotic solvent has a particularly small relative permittivity such as 1,3-dioxolane, e = 7.13 at 298K, the substrate for macrocyclic complexation is not the solvated cation but rather the ion pair. For instance, in the case of $LiAsF_6$ and 18-crown-6 dissolved in 1,3-dioxolane the Eigen-Winkler mechanism is more appropriately written as

$$LiAsF_6 + C \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} LiAsF_6 \cdots C \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} LiCAsF_6 \qquad (2)$$

to describe the two ultrasonic relaxations that were detected (ref. 10).

RECENT DEVELOPMENTS

A recently completed ultrasonic absorption study (ref. 11) of the macrocycles 18-crown-6 (1), diaza-18-crown-6 or Kryptofix-22 (2), 222-cryptand (3), and $(C_{10}H_{21})_2$-diaza-18-crown-6 or Kryptofix 22-DD (4) in acetonitrile and in methanol



1 2 3 4

is an important first step to an understanding of the metal ion binding kinetic properties of these macrocycles. 18-crown-6 undergoes a conformational change in acetonitrile at a frequency of about 80 MHz much as it does in water (ref. 12) while in methanol the relaxation is much faster. The cryptand 3 also experiences only one detectable relaxation in acetonitrile and other aprotic solvents but displays two relaxations in protonated solvents such as methanol (ref. 13). These two cryptand relaxations are attributed to rotation of the two nitrogen atoms of 3 associated with rearrangements of the ethereal chains and changes in solvation of this macrocycle. If the lone pair of electrons of one of the nitrogen atoms points into the macrocycle cavity, the conformation at that nitrogen is said to be endo. Thus the postulated reaction scheme that accounts for the cryptand 3 ultrasonic absorption data is

$$\text{endo-endo} \rightleftarrows \text{endo-exo} \rightleftarrows \text{exo-exo} \qquad (3)$$

It must then be assumed that the protic solvents give rise to a more even distribution of the cryptand 3 among the three species thus facilitating the detection of two ultrasonic relaxation processes. Two ultrasonic relaxation processes are detected for Kryptofix 22 2 in both acetonitrile and methanol that are also accounted for by eq. 3. Judging from differences in the ultrasonic spectra of the diaza crowns 2 and 4 in methanol, the long alkyl chains of 4 slow considerably the rotation of the nitrogen atoms in 4 compared to those in 2.

Infrared spectral data can enhance our understanding of conformational changes of macrocycles in solution like those described above. For instance, spectra in the ~800-900 cm^{-1} region for 18-crown-6 dissolved in acetonitrile show three bands at 857, 842.5 and 835 cm^{-1} that are dominated by the comparatively large 842.5 cm^{-1} peak (ref. 14). Predominance of one configuration of the macrocycle is consistent with the observation in acetonitrile of only one ultrasonic relaxation arising from an equilibrium between the dominant form and one of the other two configurations. Infrared spectral data obtained from ~0.1 M concentrations of $NaClO_4$ and NaSCN dissolved in acetonitrile also show that contact ion pairs are present in this comparatively low donor number (DN = 14.1) solvent (ref. 14). However, ultrasonic absorption data for sodium perchlorate, sodium tetraphenylborate and sodium thiocyanate dissolved with 18-crown-6 in acetonitrile are quite similar indicating that the sodium cation-crown ether interaction is stronger than the cation-anion interaction even in this low donor number solvent (ref. 14). These are good examples of the valuable synergism that arises from applying both ultrasonic and infrared spectral techniques to a given dissolved macrocyclic system.

Stopped-flow techniques had been used successfully for a long time to study the comparatively slow complexation of metal ions by cryptands (ref. 15). Hence we were pleased and a little surprised at first by the rich complexity of the ultrasonic absorption spectra of alkali metal cations dissolved with 222 cryptand in dry propylene carbonate (ref. 4). It turns out that one is able to observe two relaxation processes corresponding to first-order or pseudo-first-order rate processes. They are attributed to a process like that shown in eq. 3 wherein the cryptate undergoes successive intramolecular rearrangements, probably involving nitrogen rotation, with the coordinated metal ion never detaching from the macrocycle. When the diaza compound 2 reacts with silver cation in acetonitrile the ultrasonic absorption results are similar to those obtained for silver cation and compound 3 in the same solvent (ref. 16). Evidently, the presence and geometrical positioning of the nitrogen atoms of the two ligands, rather than the presence or absence of a third ethereal chain, are the key factors in the dynamics that are detected by ultrasonic absorption. Many additional details of the mechanism of complexation of metal ions by macrocycles could be distilled from recently published ultrasonic absorption studies.

Nuclear magnetic resonance data (ref. 17) indicate that for solutions in solvents of low donor number such as acetonitrile and nitromethane (DN = 2.7) dissociation of a metal-macrocycle complex is not initiated by the solvent molecule S as in eq. 4

$$(MC)^+ + S \rightleftarrows \ldots \rightleftarrows MS^+ + C \qquad (4)$$

and as we have inferred from the ultrasonic absorption experiments described above. Instead NMR data (ref. 17) are consistent with the initiation of dissociation by metal cations in excess as in the following exchange reaction

$$(MC)^+ + {}^*M^+ \rightleftarrows ({}^*MC)^+ + M^+ \qquad (5)$$

Mechanism 5 is particularly important for large crown ethers such as dibenzo-24-crown-8 and dibenzo-30-crown-10. For instance, Shamsipur and Popov (ref. 18) used cesium-133 NMR to study the interaction of the cesium cation with dibenzo-30-crown-10 in nitromethane, acetonitrile, propylene carbonate and methanol. At temperatures below 263 K the exchange mechanism of eq.5 dominates in the last three solvents. From thermodynamic data on crown ether complexation of metal ions in nonaqueous solvents (ref. 19) it is evident that the stability constant for a metal ion-crown ether complex increases as the temperature decreases. Thus as temperature decreases there is less affinity between the solvent S and the $(MC)^+$ complex necessary to initiate reaction 4. If another potential attacker of $(MC)^+$ is present such as M^+ in excess (or anion X^- in excess), reaction 5 or its analogue reaction 6

$$(MC)^+ + X^- \rightleftarrows (MX) + C \qquad (6)$$

could become important.

Ultrasonic absorption techniques cannot detect a process such as reaction 5 since the molar volumes and molar enthalpies are unchanged as reactants proceed to products. In non-aqueous media of low permittivity ultrasonics even fail to detect the initial second order step of reaction 1 because the stability constant is so large. What ultrasonic methods detect instead are the intramolecular changes of $M^+...C$, MC^+ and $(MC)^+$ under the influence of an adiabatic pressure wave. The NMR method also fails to detect the initial second order step of reaction 1 because the forward process is too fast; it can only detect the initial attack of the reverse process of reaction 1 or, if you like, the initial attack of reactions 4, 5 and 6. Because of these inherent differences in the two methods and particularly because of the difference in their accessible time scales it is not certain that the results obtained by these two methods on a system such as cesium cation plus dibenzo-30-crown-10 in acetonitrile at low temperatures can be checked against one another very effectively. However, the experiments certainly should be carried out.

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REFERENCES

1. J.E. Stuehr in Investigations of Rates and Mechanisms of Reactions (Fourth Edition), ed. C.F. Bernasconi (Techniques of Chemistry, Vol. VI, Part II), Chap. 6, Wiley, New York (1986).
2. E. Grell, T. Funck and F. Eggers in Membranes: A Series of Advances, ed. G. Eisenman, Marcel Dekker, New York, Vol. 3, pp. 1-126 (1975).
3. L.J. Rodriguez, G.W. Liesegang, M.M. Farrow, N. Purdie and E.M. Eyring, J. Phys. Chem. 82, 647-650 (1978) and references cited therein.
4. See e.g. H. Schneider, K.H. Richmann, T. Funck, P. Firman, F. Eggers, E.M. Eyring and S. Petrucci, J. Phys. Chem. 92, 2798-2804 (1988).
5. J.-P. Gabano, ed., Lithium Batteries, Academic Press, New York (1983).
6. M. Eigen and R. Winkler in The Neurosciences: Second Study Program, ed. F.O. Schmitt, Rockefeller University Press, New York, pp. 685-696 (1970).
7. See e.g. M. Eigen and R.G. Wilkins, A.C.S. Sym. Ser. 49, 55-80 (1965).
8. W. Wallace, E.M. Eyring and S. Petrucci, J. Phys. Chem. 88, 6353-6356 (1984).
9. S. Petrucci, R.J. Adamic and E.M. Eyring, J. Phys. Chem. 92, 2781-2789 (1988).
10. M. Xu, N. Inoue, E.M. Eyring and S. Petrucci, J. Phys. Chem. 92, 2781-2789 (1988).
11. L.J. Rodriguez, E.M. Eyring and S. Petrucci, J. Phys. Chem., in press.
12. G.W. Liesegang, M.M. Farrow, L.J. Rodriguez, R.K. Burnham and E.M. Eyring, Intl. J. Chem. Kinetics 10, 471-487 (1978).
13. F. Eggers, T. Funck, K.H. Richmann, H. Schneider, E.M. Eyring and S. Petrucci, J. Phys. Chem. 91, 1961-1967 (1987).
14. L.J. Rodriguez, E.M. Eyring and S. Petrucci, J. Phys. Chem., submitted for publication.
15. See e.g. B.G. Cox, J. Garcia-Rosas, H. Schneider and Ng. van Truong, Inorg. Chem. 25, 1165-1168 (1986).
16. L.J. Rodriguez, E.M. Eyring and S. Petrucci, in preparation.
17. See e.g. E. Schmidt and A.I. Popov, J. Am. Chem. Soc. 105, 1873-1878 (1983); A. Delville, H.D.H. Stover and C. Detellier, J. Am. Chem. Soc. 109, 7293-7301 (1987).
18. M. Shamsipur and A.I. Popov, J. Phys. Chem. 92, 147-151 (1988).
19. J.D. Lamb, R.M. Izatt, J.J. Christensen and D.J. Eatough in Coordination Chemistry of Macrocyclic Compounds, ed. G.A. Melson, Plenum, New York, pp. 145-217 (1979).