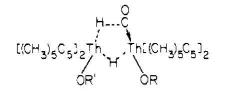
argue that *intermolecular* hydride transfer to coordinated CO[21] is not important in eq 7. Exchange is only observed between hydride and formyl protons of species bearing the same alkoxide group, whereas intermolecular hydride transfer would reasonably be expected to permute all hydride environments. Further studies of the kinetic/thermodynamic aspects of the migratory CO insertion process and the chemical reactivity of organoactinide formyls are in progress.

Acknowledgment. We thank the National Science Foundation (CHE8009060) for generous support of this research and Joseph F. Lomax for experimental assistance.

---

(20) Gjaldbaek, J. C.; Andersen, E. K. *Acta Chem. Scand.* **1965**, *8*, 1398-1413 and references therein.

(21) Presumably via a hypothetical transition state such as



Molecular models suggest that such structures would be prohibitively high in energy.

Formation Constants of Ion Pair-Ligand Complexes. Application of Crown Ether Network Polymers

Roger Sinta and Johannes Smid*

Chemistry Department
College of Environmental Science and Forestry
State University of New York, Syracuse, New York 13210

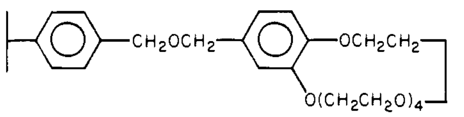
Received June 17, 1981

Crown ethers, cryptands, podands, and other cation-binding ligands, when used in anion-activated catalysis or mediated ion transport, are usually operating in an apolar environment where ionic species tend to associate into ion pairs. Quantitative information on complexation between ligands and ion pairs in apolar solvents (e.g., dioxane, toluene) is frequently hard to obtain because of the large formation constants of the complexes. We now wish to report that crown ether network polymers can serve as reliable probes in the study of ion pair-ligand complexes, including the determination of their association constants in apolar media. Moreover, the measurements can also furnish quantiative information on ion pair binding to crown ether network polymers, materials employed in anion-activated catalysis[1-3] and the separation of solutes.[4,5] Crown ether resin I, synthesized from 2% cross-linked chloromethylated polystyrene and [(hydroxymethyl)benzo]-18-crown-6 is added to a solution of a metal picrate in dioxane, conditions being such that nearly all picrate salt is bound to the insoluble crown polymer (crown to picrate ratio ~40). Addition of a soluble ligand (e.g., 18-crown-6, cryptand 2.2.2) releases the network-bound salt into the solution according to reaction 1 where the starred species are network bound. If f_1

$$\mathrm{Pi^-,M^+,Cr^*} + \mathrm{L} \underset{K}{\rightleftarrows} \mathrm{Cr^*} + \mathrm{Pi^-,M^+,L} \tag{1}$$

is the fraction of the ligand L bound to the picrate salt ($f_1 = \mathrm{Pi^-,M^+,L/L_0}$) and f_2 the fraction of the network crown bound to the salt ($f_2 = \mathrm{Pi^-,M^+,Cr^*/Cr_0^*}$), then the following relationship holds.

$$[(1/f_2) - 1] = \mathrm{K}[(1/f_1) - 1] \tag{2}$$



I

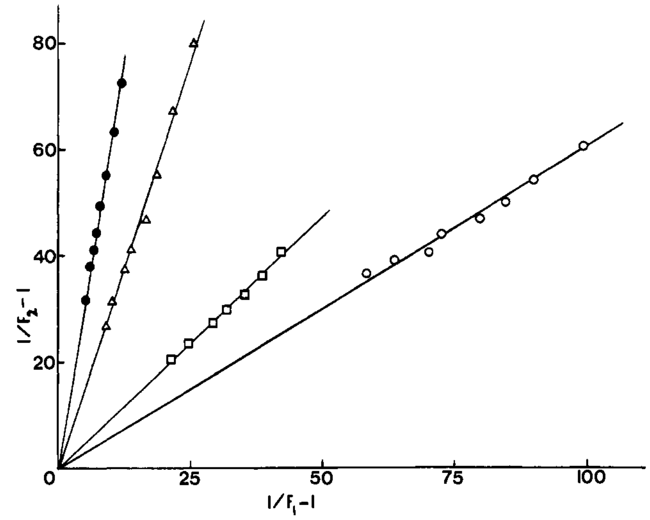


Figure 1. Plots of $(1/f_2) - 1$ vs. $(1/f_1) - 1$ in dioxane for the equilibrium $\mathrm{Pi^-,K^+,Cr^*} + \mathrm{L} \rightleftarrows \mathrm{Pi^-,K^+,L} + \mathrm{Cr^*}$ (see text) for different ligands L: (●) 18-crown-6; (△) dicyclohexano-18-crown-6 (□) 4'-(methylbenzo)-18-crown-6; (○) (dimethyldibenzo)-18-crown-6.

Table I. Association Constants, K_L, of Macroheterocyclic Ligands to Potassium Picrate in Dioxane at 25 °C

ligand	K	$K_L \times 10^{-5}$, M^{-1}
(dimethyldibenzo)-18-crown-6	0.596	1.03
4'-(methylbenzo)-18-crown-6	0.908	1.56
dicyclohexyl-18-crown-6	3.13	5.38
18-crown-6	5.62	9.67
cryptand 2.2.2.	1230	2000

Since the total concentrations of picrate ($\mathrm{Pi_0^-}$), ligand ($\mathrm{L_0}$), and crown ($\mathrm{Cr_0^*}$, in equivalents) are known, f_1 and f_2 can be determined by measuring spectrophotometrically the concentration of $\mathrm{Pi^-,M^+,L}$ in dioxane, since $\mathrm{Pi^-,M^+Cr^*} = \mathrm{Pi_0^-} - \mathrm{Pi^-,M^+,L}$. Figure 1 depicts plots of $(1/f_2) - 1$ vs. $(1/f_1) - 1$ for four different crown ethers. K values calculated from these plots are collected in Table I, including the value for cryptand 2.2.2. Note that K for 4'-(methylbenzo)-18-crown-6 is 1.03. This implies that the cation affinity of this crown is essentially the same whether anchored to a dioxane-swollen network or a free ligand in dioxane. Increased ion pair loading or higher crown densities on the network (I contains on the average 1 crown ether for 11 monomer units) may well result in differences in cation affinities. Also, preliminary data in THF as solvent yield K about 4.0, indicating a decreased affinity of the network-bound benzo-18-crown-6 relative to that of the free ligand.

Equilibrium 1 can be analyzed in terms of reactions 3 and 4

$$\mathrm{Cr^*} + \mathrm{Pi^-,M^+} \underset{K_N}{\rightleftarrows} \mathrm{Pi^-,M^+,Cr^*} \tag{3}$$

$$\mathrm{L} + \mathrm{Pi^-,M^+} \underset{K_L}{\rightleftarrows} \mathrm{Pi^-,M^+,L} \tag{4}$$

where

$$K = K_L/K_N \tag{5}$$

The formation constants, K_L, for ion pair-ligand complexes in solution can be calculated from (5) if K_N in known. The latter represents the binding constant of an ion pair to the crown network

---

(1) S. L. Regen, *Angew. Chem., Int. Ed. Engl.*, **18**, 421 (1979).

(2) H. Molinari, F. Montanari, and P. Tundo, *J. Chem. Soc., Chem. Commun.*, 639 (1977).

(3) L. J. Mathias and J. B. Canterberry, *Polymer Prepr.*, **22** (1), 38 (1981).

(4) E. Blasius, K. P. Janzen, W. Adrian, G. Klautke, R. Lorscheider, P. G. Maurer, V. B. Nguyen, T. Nguyen Tien, G. Scholten, and J. Stockemer, *Z. Anal. Chem.*, **284**, 337 (1977).

(5) K. Kimura, M. Nakajima, and T. Shono, *Anal. Lett.*, **13** (A9), 741 (1980).

0002-7863/81/1503-6962$01.25/0

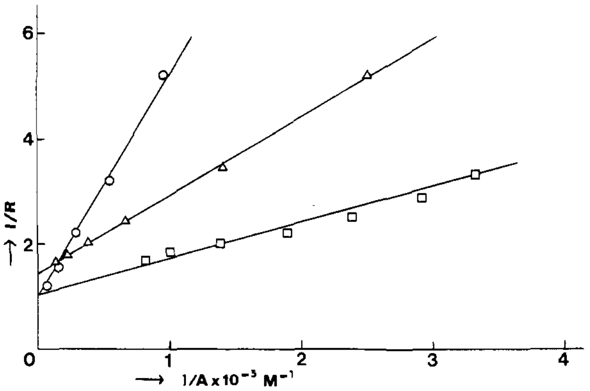


Figure 2. Binding of picrate salts to a crown ether network polymer in dioxane at 25 °C (0.70 mequiv of benzo-18-crown-6 per gram of polystyrene network): (○) sodium picrate; (□) potassium picrate; (△) cesium picrate.

polymer I. It can be obtained by equilibrating the crown resin with a picrate solution in dioxane. The binding in such a system can be described by a rearranged form of the Langmuir adsorption isotherm

$$1/R = 1/n + 1/(nK_NA) \qquad (6)$$

where $1/R = Cr_0^*/Pi^-,M^+,Cr^*$, A is the free picrate concentration in solution which can be measured, K_N is the intrinsic binding constant, and $1/n$ denotes the number of crown units in the Pi^-,M^+,Cr^* complex (usually $1/n = 1$ or 2). Plots of $1/R$ vs. $1/A$ for network I in dioxane are depicted in Figure 2. The intercept for Cs^+ deviates from 1, and the value $1/n = 1.40$ suggests the presence of 2:1 crown–Cs^+ complexes on saturation of the network. Such complexes have been found in linear polymers with the benzo-18-crown-6 ligand.[6] The K_N values calculated from the slopes of Figure 2 are 2.58×10^4 (Na^+), 1.72×10^5 (K^+), and 6.55×10^4 M^{-1} (Cs^+, assuming a 1:1 complex).

K_L values for Pi^-,K^+ can now be computed from eq 5 and $K_N = 1.72 \times 10^5$ M^{-1}. They are listed in Table I. A direct spectrophotometric measurement for 4′-(methylbenzo)-18-crown-6 yielded $K_L = 1.7 \times 10^5$ M^{-1}, close to the value found by the network method (the spectral method is rather inaccurate since the shift in λ is only 10 nm). Comparisons with available literature data indicate that the order of K_L values for the four crown ligands of Table I is solvent and anion dependent. Most data in apolar solvents have been derived from extraction experiments which yield composite extraction equilibrium constants. An exception are the interesting ^1H NMR measurements of Reinhoudt et al. in $CDCl_3$[7,8] although this method requires high complex concentrations. A distinct advantage of the method described above is the low ion pair concentration (10^{-4}–10^{-5} M) which minimizes ion pair aggregation.[9] A direct measurement of equilibrium 4 is difficult since Pi^-,M^+ and Pi^-,M^+,L often have nearly identical spectra (Pi^-,M^+,L in dioxane is a tight ion pair for most crown ligands). Cryptand 2.2.2. forms a cryptated loose ion pair (λ_m changes from 349 to 380 nm), but the value of K_L is very high (see Table I) which makes a direct measurement difficult.

The K_N data are important in evaluating the cation binding behavior of crown ether networks as a function of variables such as spacing between crown units (especially important in systems where the cation complexes simultaneously with two crown units), the length and structure of the chain connecting the macrocycle to the polymer, the cross-linking density, presence of comonomer substituents, etc. For ion pairs with anions that have less favorable optical absorption spectra than picrate salts, competitive binding can be employed, i.e., $Pi^-,M^+,Cr^* + A^-,M^+ \rightleftarrows Pi^-,M^+ + A^-,M^+,Cr^*$. The equilibrium constant of this reaction, together with the K_N value for the picrate salt, yields the binding constant K_N for the A^-,M^+ ion pair to the network. Preliminary data for the BPh_4^- anion shows that the binding of this alkali salt to the crown network is much larger than for the corresponding alkali picrates. Similar competitive equilibria in solution can be used to arrive at K_L values in apolar solvents for anions other than picrates.

The above method can also be used to study interactions of ion pairs with additives such as water. For example, small amounts of water added to Pi^-,M^+,Cr^* in dioxane release the picrate and form $Pi^-,M^+,(H_2O)_n$. Networks containing cryptand or podand (e.g., glyme) ligands can also be used in the ion pair studies. Complications will arise in solvents where free ion dissociation becomes significant, since complex formation constants between ligands and free cations are often much higher than between ligands and ion pairs.[10] Some deviations from linearity in the adsorption plots of Figure 2 have been observed when tetrahydrofuran is used as solvent, probably as a result of partial dissociation of the Pi^-,M^+,L ion pairs into free ions.

Acknowledgment. We gratefully acknowledge the financial support of this research by the National Science Foundation (Grant CHE 7905890).

---

[6] S. Kopolow, T. E. Hogen Esch, and J Smid, *Macromolecules* 6, 133 (1973).

[7] D. N. Reinhoudt, R. T. Gray, F. de Jong, and C. J. Smit, *Tetrahedron Lett.*, 563 (1977).

[8] R. T. Gray and D. N. Reinhoudt, *Tetrahedron Lett.*, 2109 (1975).

[9] U. Takaki, T. E. Hogen Esch, and J. Smid, *J. Am. Chem. Soc.*, 76, 2152 (1972).

[10] M. Bourgoin, K. H. Wong, J. Y. Hui, and J. Smid, *J. Am. Chem. Soc.*, **97**, 3462 (1975).

Efficient Electron Channel through Self-Aggregation of Cytochrome c_3 on an Artificial Membrane

Iwao Tabushi* and Takako Nishiya

Department of Synthetic Chemistry
Kyoto University, Kyoto 606, Japan

Tatsuhiko Yagi

Department of Chemistry
Shizuoka University, Shizuoka 422, Japan

Hiroo Inokuchi

Institute for Molecular Sciences
Myodaiji, Okazaki 444, Japan

Received March 16, 1981

Among many known heme proteins, cytochrome c_3 (abbreviated as c_3) is undoubtedly one of the most interesting. It has a unique structure to keep four heme units in a single protein[1] of moderate molecular weight (e.g., ca. 14 000 for Desulfovibrio vulgaris Miyazaki[1]) in which each Fe–Fe distance is not too long, ranging between 11.5 and 17.9 Å for D. vulgaris or 10.9–17.3 Å for D. desulfuricans[2,3] and interacting with each other as is apparent from the Mössbauer[4] or EPR[5] spectrum. This electron carrier also has a unique property to conduct electriicity (1.8×10^{-2} Ω^{-1} cm^{-1}) in a solid-state film.[6] This conductivity strongly indicates that this protein has a very strong intermolecular interaction with surrounding proteins.

However, nothing has been clarified about the nature of these significant intramolecular and intermolecular heme–heme interactions, and more mechanistic investigation seems to be necessary and important.

---

[1] Yagi, T.; Maruyama, K. *Biochim. Biophys. Acta* **1971**, *243*, 214–224.

[2] Higuchi, Y.; Yasuoka, N.; Kakudo, M; Yagi, T.; Inokuchi, H. *J. Biochem.* **1981**, *89*, 1659–1662.

[3] Hauser, R.; Pierrot, M.; Frey, M.; Payan, F.; Astier, J. P.; Bruschi, M.; LeGall, J. *Nature (London)* **1979**, *282*, 806–810.

[4] Ono, K.; Kimura, K.; Yagi, T.; Inokuchi, H. *J. Chem. Phys.* **1975**, *63*, 1640–1642.

[5] LeGall, J.; Bruschi-Heriaud, M.; DerVartanian, D. V. *Biochim. Biophys. Acta* **1971**, *234*, 499–512.

[6] Nakahara, Y.; Kimura, K.; Inokuchi, H.; Yagi, T. *Chem. Lett.* **1979**, 877–880.

0002-7863/81/1503-6963$01.25/0