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PS5.44 — TH

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SUBSTITUENT EFFECTS ON THE DISSOCIATION KINETICS OF HEAVY METAL ION CRYPTATES

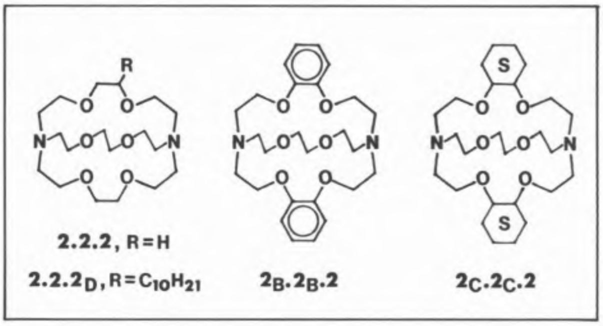
The dissociation kinetics of the cryptates of 2.2.2, $2.2.2_D$, $2_B.2_B.2$ and $2_C.2_C.2$ with Tl^+ and Pb^{2+} have been studied in water and methanol-water (90:10) at 25.0°C. The dissociation reactions generally displayed parallel solvolytic (k_d) and acid-catalyzed (k_H) pathways consistent with the rate law:

$$-d[MCryp^{n+}]/dt = (k_d + k_H[H^+])\,[MCryp^{n+}].$$

The introduction of a decyl side chain ($2.2.2_D$) produced only minor variations in the values of k_d and k_H when compared with the parent cryptand, 2.2.2. Larger effects are observed with the dibenzo-derivative ($2_B.2_B.2$) with Tl^+ and for the dicyclohexano-derivative ($2_C.2_C.2$) with both Pb^{2+} and Tl^+. The rate constants for the uncatalyzed and acid-catalyzed pathways in methanol-water decrease by 20- to 200-fold compared with the corresponding values obtained in water.

INTRODUCTION

The macrobicyclic polyoxa-diamines (cryptands) introduced by LEHN and co-workers form stable complexes with alkali-, alkaline-earth- and heavy metal cations [1,2]. The relative rigidity of these ligands results in peak type selectivity related to the ratio of ligand cavity to metal cation diameter. In addition to cavity size, parameters such as donor atom type and ligand backbone substituents also affect the complexation properties of the cryptands [1-3]. The introduction of hydrophobic decyl-, benzo-, and cyclohexano-moieties into the cryptand (see Fig. 1) structure increases their ability to solubilize salts in non-polar media [4] and membranes [5,6]. In view of the demonstrated ability of the parent compound, cryptand 2.2.2, to enhance elimination of toxic heavy metal ions [7,8] an evaluation of substituent effects on the complexation properties with Pb^{2+} and Tl^+ was carried out and the results are reported in this communication.



2.2.2, R=H

$2.2.2_D$, R=$C_{10}H_{21}$ **$2_B.2_B.2$** **$2_C.2_C.2$**

Fig. 1
Structures of 2.2.2 Cryptands

EXPERIMENTAL

Cryptands 2.2.2, $2.2.2_D$, $2_B.2_B.2$ and $2_C.2_C.2$ were obtained from E. Merck and used without further purification. Stock cryptand solutions were analyzed spectrophotometrically [9]. Kinetic studies were carried out by mixing equal volumes of the appropriate cryptate ($3.0\text{-}7.0 \times 10^{-5}$ M) with a solution of known $HClO_4$ concentration (1.12-74.5 mM). The reactions were monitored in the wavelength region of 245-255 nm on either a Durrum stopped-flow or a Hitachi 80-100 spectrophotometer. The cell temperature was maintained at 25.0 (±0.1)°C using a thermostated water bath.

All reactions were pseudo-first-order and rate constants were obtained using standard least squares technique.

RESULTS AND DISCUSSION

In strongly acidic media the cryptate complexes dissociate via parallel uncatalyzed and proton-catalyzed pathways. The data are consistent with the rate law:

$$-d[MCryp^{n+}]/dt = (k_d + k_H[H^+])[MCryp^{n+}] \qquad (1)$$

where $M^{n+} = Tl^+$ or Pb^{2+} and k_d and k_H are the rate constants for the uncatalyzed and acid-catalized pathways, respectively. The influence of ionic strength on k_H was accounted for by the relationship:

$$k_{obs} = k_d + k^{o}_{H}[H^+]\gamma_H\gamma_{MC}/\gamma_{\neq} \qquad (2)$$

where k^{o}_{H} is the rate constant value at zero ionic strength and γ_H, γ_{MC} and $\gamma_{\neq}$ are the activity coefficients of the proton, cryptate and transition-state complex, respectively. Values of γ_i were calculated using the Davies equation [10]. The values of k_d and k^{o}_{H} obtained from plots of equation (2) are listed in Table 1.

The values of k_d in methanol-water are less than the corresponding values in water as expected [11]. In methanol-water the k_d values of the thallium cryptates increase in the sequence: $2.2.2 < 2.2.2_D \ll 2_B.2_B.2 < 2_C.2_C.2 \ll 2.2\ C_8$. The introduction of the decyl-side chain has little effect on the dissociation kinetics of the Tl^+ and Pb^{2+} complexes in agreement with the results reported for the analogous alkali-cation cryptates [12]. The introduction of the benzo-groups into the cryptand structure has three effects; (i) increased rigidity resulting in a smaller effective cavity, (ii) decreased donor ability of the catechol-ether oxygen atoms and (iii) increased shielding of the cation from the solvent [1]. These factors combine to weaken the cryptand with Tl^+ [13] and this decrease in stability is reflected in the large increase in the value of k_d. Similar behavior has been reported for the Ba^{2+} cryptates of 2.2.2 and $2_B.2_B.2$ [14]. Saturation of the rings has little effect on the value of k_d compared to the value for $2_B.2_B.2$ with thallous ion in methanol-water. A much larger effect is noted when the k_d values for the lead ion cryptates of $2_C.2_C.2$ and 2.2.2 are compared. This may be due to the higher charge of Pb^{2+} and the increased shielding provided by cyclohexano-groups which would hinder solvation of the cryptate. The trends for the k^{o}_{H} values of the cryptates are not as distinct as those for the k_d values. However, for both cations, the k^{o}_{H} values for $2_C.2_C.2$ are much larger than those of the other cryptands. The values of k^{o}_{H} are 50- to 200-fold lower in methanol-water than the corresponding values in water, with the larger difference being

Table 1

Rate Constant Values for Acid-Catalyzed Dissociation of Tl^+ and Pb^{2+} Cryptates at 25 °C [a)]

		Tl^+		Pb^{2+}	
Ligand	Solvent [b)]	k_d, sec^{-1}	k^{o}_{H}, $M^{-1}\ sec^{-1}$	k_d, sec^{-1}	k^{o}_{H}, $M^{-1}\ sec^{-1}$
2.2.2	H_2O [c)]	5.5 ± 0.6	1050 ± 95	1.8×10^{-5}	0.71
	M/W	0.10 ± 0.01	26 ± 1	$< 10^{-5}$	4.0×10^{-3}
	M/W [d)]	0.12 ± 0.01	20 ± 1		
$2.2.2_D$	H_2O	—	—	$< 10^{-4}$	0.44
	M/W	0.45	37	$< 10^{-5}$	3.0×10^{-3}
$2_B.2_B.2$	H_2O	102	4100	$< 10^{-4}$	0.057
	M/W	6.2	63	—	—
$2_C.2_C.2$	H_2O	—	—	~ 0.002	13.3
	M/W	17.7	3500	$\sim 3 \times 10^{-5}$	0.056

a) k_d values at $\mu = 0.1$ (Et_4NClO_4), k^{o}_{H} values at $\mu \to 0$.

b) M/W = methanol-water (90:10).

c) [15].

d) [16].

observed for the lead cryptates. This result is most likely a consequence of the lower dielectric constant of the methanol-water mixture compared with water.

ACKNOWLEDGEMENTS

This work was supported in part by the Petroleum Research Fund, administered by the American Chemical Society and the University of Oklahoma Research Council.

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PS5.45 — MO

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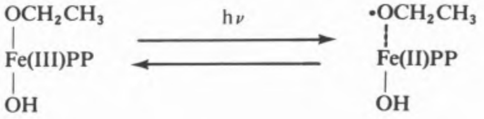
PHOTOCHEMISTRY OF IRON(III) PROTOPORPHYRIN IX IN OXYGENATED ALKALINE AQUEOUS ETHANOL. EVIDENCE FOR SUPEROXIDE RADICAL FORMATION AND ITS INVOLVEMENT IN THE PORPHYRIN DEGRADATION

The interest for the formation of superoxide in biological aerobic processes is on steady increase in connection with the auto-oxidation of dioxygen carrier hemoproteins as well as with its toxic effect on living systems.

In recent years, a number of very interesting studies on both the mechanism of formation of superoxide and its reactivity with respect to biological substrates have been reported [1].

We have recently published an ESR-spin trapping investigation on the photochemical behaviour of Fe(III) Protoporphyrin IX chloride (Fe(III)PPCl) in oxygenated water-ethanol mixed solvents [2]. The results obtained in that study allowed us to conclude that Fe(II) porphyrin and an ethoxy radical were formed in the primary photochemical process and that the oxygen interacted somehow with Fe(II) thus hindering a rapid cage back electron transfer. The mechanism proposed is reported in Scheme 1.

Scheme 1



$$\begin{array}{c} OCH_2CH_3 \\ | \\ Fe(III)PP \\ | \\ OH \end{array} \overset{h\nu}{\rightleftarrows} \begin{array}{c} \cdot OCH_2CH_3 \\ \vdots \\ Fe(II)PP \\ | \\ OH \end{array} \qquad (1)$$