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Kinetics of Cadmium Porphyrin–Zinc Ion Electrophilic Exchange Reactions: An Isokinetic Relationship

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There is relatively little quantitative information available concerning the mechanisms of electrophilic exchange between one metal ion and another complexed in a porphyrin molecule [1]. Kinetic studies on the Cu/Zn–P reaction with two water soluble porphyrins [2, 3] indicated rate laws first order in each

$$M_A^{2+} + M_B\text{–}P \longrightarrow M_B^{2+} + M_A\text{–}P \qquad (1)$$

reactant, with no rate inhibition by the replaced metal ion. The Zn/Hg–TPP (TPP is tetraphenylporphyrin) system has a similar rate law [4], and the occurrence of seven isosbestic points during the course of the reaction and the relative slowness of the Zn/H_2–TPP incorporation reaction (compared to the Zn/Hg–TPP exchange), argued for a direct exchange Zn–P–Hg pathway, as opposed to a predissociation into the free base H_2–TPP followed by a subsequent complexation. The replacing and replaced metal ions were considered to be on opposite sides of the porphyrin plane, in line with crystal structure results of several bi-metallated porphyrins [5].

The dependence of the exchange rate on porphyrin basicity was investigated in the Cu/Zn–TPP systems using various disubstituted deuteroporphyrins and synthetic *ms*-porphyrins [2]. Unfortunately, reasonable rates could only be obtained by working in refluxing pyridine on the time scale of days, and the resulting separations were both tedious and inaccurate. Coupled with the fact that most of the deuteroporphyrin types decomposed to a large extent under the reaction conditions, a more ideal system was sought. To this end, we report a study of the Zn/Cd–P exchange in pyridine at ambient temperatures, using fourteen different porphyrins. Relative rates were done for the modified natural porphyrins, and activation parameters were obtained for the *ms*-synthetic derivatives.

Experimental

All porphyrins were obtained from Man-Win Coordination Chemicals, Washington, D.C. The cadmium porphyrins were prepared by literature methods [6]. The Zn/Cd–P reactions were followed spectrophotometrically in pyridine containing 0.5 *M* water as the solvent, and zinc perchlorate was analyzed by EDTA titrations. The cadmium and zinc porphyrins were stable for days in the solvent, in which both metalloporphyrins are in their monopyridinate foms [7]. Zinc acetate reacted approximately 150 times slower than zinc perchlorate.

Results and Discussion

The Zn/Cd–P reactions were found to be unidirectional and first order in each ractant. Activation parameters were calculated from rate data taken from 15 °C to 37 °C for the *ms*-porphyrins. The rates of zinc incorporation into the corresponding free base *ms*-porphyrins were measured at 25 °C, and the results are presented in Table I. Table II contains rate data for the Zn/Cd–P reactions with modified natural porphyrins at 25 °C.

For the *ms*-porphyrins, the rates of the Zn/Cd–P exchange reactions are from 600 to 6700 times faster than the corresponding Zn/H_2–P incorporation reac-

TABLE I. Rate Data for *Meso*-substituted Cadmium–Porphyrin Exchange Reactions with Zinc.

Cd–Porphyrin[a,b]	$\Delta H^\ddagger$ (Kcal/mol)	$\Delta S^\ddagger$ (eu)	$k_{25^\circ C}$ (M^{-1} s^{-1})	k_{exch}/k_{incor}[c]
(*p*-CH_3)–TPP	16.8	+2.1	8.3	1640
(*o*-CH_3)–TPP	14.6	−5.2	8.5	6700
(*p*-OCH_3)–TPP	13.9	−7.3	10.2	1000
(*p*-CN)–TPP	13.1	−14.0	1.2	1400
(*p*-H)–TPP	11.5	−16.4	5.7	1530
(*p*-Cl)–TPP	10.8	−21.6	1.3	600

[a] Pyridine–0.5 *M* water solvent, with $Zn(ClO_4)_2$. [b] TTP is tetraphenylporphyrin. [c] k_{exch}/k_{incor} is the ratio of the Zn/Cd–P exchange rate to the Zn/H_2–P incorporation rate at 25 °C.

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TABLE II. Rate Data for β-substituted Cadmium–Porphyrin Exchange Reactions with Zinc, 25 °C.

Cd–Porphyrin[a,b,c]	$k_{Zn/Cd–P}$ $(M^{-1}\ s^{-1})$
Etioporphyrin-I	41.8
Octaethylporphyrin	37.6
Coproporphyrin-III-TME	20.2
Uroporphyrin-I-OME	17.4
Protoporphyrin-IX-DME	14.2
Deuteroporphyrin-IX-DME	13.8
Br_2-Deuteroporphyrin-IX-DME	3.4
Diacetyldeuteroporphyrin-IX-DME	3.1

[a] Pyridine–0.5 *M* water solvent, with $Zn(ClO_4)_2$. [b] OME, TME, DME are the octa, tetra and dimethylesters. [c] Structures of the porphyrins are found in ref. 1.

tions. This shows that the free base porphyrins are not reaction intermediates; a direct exchange pathway is indicated. It is noted in Table I that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ compensate one another; the more favorable the $\Delta H^{\ddagger}$, the less favorable is $\Delta S^{\ddagger}$. Considering the (p-CH_3)–TPP and (p-Cl)–TPP complexes, and assuming $\Delta H^{\ddagger}$ (or $\Delta S^{\ddagger}$) to be the same for both metalloporphyrins, with the rate variation due to $\Delta S^{\ddagger}$ (or $\Delta H^{\ddagger}$), over a twenty five thousand fold rate difference would be predicted for the exchange reactions. Due to the compensation effect, however, the observed difference is simply a factor of 7 at 25 °C.

A plot of $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ is linear (Fig. 1), indicating the same exchange mechanism for all of the *ms*-porphyrins. The slope of the plot corresponds to the isokinetic temperature, –30 °C, the temperature at which all members of the series react at the same rate. This isokinetic behavior has important implications [8]. For example, (p-CH_3)–TPP exchanges its coordinated cadmium with zinc faster than does (p-Cl)–TPP above –30 °C, and at –30 °C, both porphyrins react at the same rate. Below –30 °C, (p-Cl)–TPP reacts faster than (p-CH_3–TPP). Thus any mechanistic conclusions as to how porphyrin basicity, Hammett or Taft substituent trends, inductive or resonance behavior, *etc.*, affect metalloporphyrin reactivity above –30 °C would be exactly opposite those made below the isokinetic temperature. Such isokinetic phenomenon has precedent in porphyrin chemistry [1]. For $Cu(OAc)_2$ incorporation into porphyrins [9] in ethanol, $T_i \approx 22$ °C, and $CuCl_2$ reactions with porphyrins [10] in DMF have $T_i \approx 57$ °C.

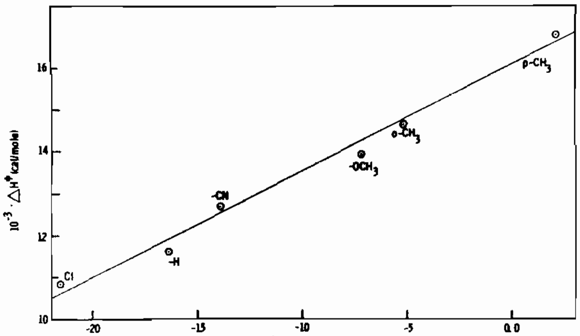

Figure 1. Plot of $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ for the Zn/Cd–P exchange reaction with Cd–*ms*-tetraphenylporphyrins and zinc perchlorate in pyridine containig 0.5 *M* water.

In conclusion, for both the modified natural porphyrins and *ms*-synthetic porphyrins at 25 °C, electron donating groups on the porphyrin periphery (which make the porphyrin more basic towards protons) increase the rate of the Zn/Cd–P exchange reactions. The rates span a thirty five fold range at this temperature, from Etioporphyrin-I the fastest to (p-CN)–TPP. The same correlation was found [11] in the acid catalyzed solvolysis reactions of zinc porphyrins; a higher porphyrin basicity leads to enhanced proton assisted solvolysis rates. Since the direct exchange pathways noted here are found to be much more rapid than the corresponding metal incorporation reactions, the occurrence of Ni^{2+} and VO^{2+} in geochemical porphyrins [12] might arise from transmetallation rather than incorporation reactions.

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