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Kinetics of Exchange Reactions of Manganese(II) Porphyrin with Zinc and Cobalt in Alkaline Environments

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The formation of manganese(II) porphyrin in aqueous environments is described. Kinetics of the exchange reaction of manganese(II) porphyrin with zinc and cobalt are reported in the ammoniacal medium. For the zinc reaction Zn^{2+} and $Zn–NH_3^{2+}$ contribute to the exchange and have rate constants of 3.3 M^{-1} S^{-1} *and 33.0* M^{-1} S^{-1} *respectively at 25 °C. These rate constants are greater than the corresponding values of zinc incorporation into this porphyrin in ammoniacal medium. For the cobalt reaction the species contributing to the exchange are $Co–NH_3^{2+}$ and $Co(NH_3)_2^{2+}$ with rate constants of 1.16* M^{-1} S^{-1} *and 0.67* M^{-1} S^{-1} *respectively at 25 °C. Activation parameters indicated a pre-equilibrium having favourable entropy for the exchange reaction of zinc.*

Introduction

The most stable of the manganese porphyrin complexes are that of the Mn(III) [1], and a sizable body of literature now exists for these complexes [2]. As a continuation of our work on the Mn(III) porphyrin [3] (MnP) we were interested in the formation, stability and further coordination capacity of the manganese(II) porphyrin complexes. The *in situ* formation and spectra of the Mn(II) hematoporphyrin has been reported [1]; however, in aqueous environments this species is highly unstable. We report here, the formation of the Mn(II) porphyrin in a relatively stable form and its exchange behaviour with metal ions like Zn^{2+} and Co^{2+}. This is an extension of our preliminary report of the exchange with zinc [4] ion. The water soluble porphyrin referred to here is the one prepared by the addition of four ethylene diamine molecules to protoporphyrin IX [3].

Experimental

Preparation of the Mn(II) Porphyrin

The starting material is the manganese(III) porphyrin prepared by methods reported earlier [3, 5]. The reducing agent used was sodium dithionite [1] in the alkaline condition. Preliminary experiments of the reduction of Mn(III)P in different buffers showed varying degrees of stability of the Mn(II)P. In the phosphate and acetate medium the Mn(II)P decomposed fast, in the imidazole buffer the Mn(II)P changed to the Mn(III)P within minutes. In the ammonia buffer the Mn(II)P was quite stable. The spectra of the Mn(III)P and the Mn(II)P in ammoniacal environments are given in Fig. 1.

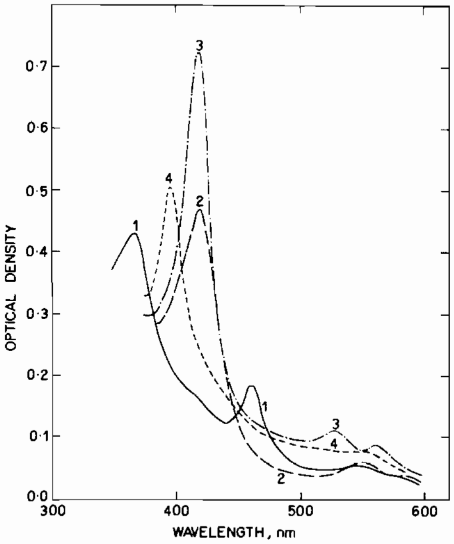

Fig. 1. Spectra of reduced manganese and cobalt porphyrins by sodium dithionite in ammoniacal environments. (———) Mn(III)P; (– – – –) Mn(II)P; (– · –) Co(III)P; (· · ·) Co(II)P.

Exchange kinetics with metal ions like Zn^{2+}, Co^{2+} and Cu^{2+} showed that the former two ions exchange the ligand from Mn(II)P in rates measurable by spectrophotometry, while the Cu^{2+} ion converts the complex to the Mn(III)P form almost instantaneously. The ammonia medium has the added advantage that the exchanging metal ions of Zn^{2+} and Co^{2+} could be kept in solution without the

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problem of precipitation in the alkaline environments where the Mn(II)P is produced.

Kinetic Studies

The exchange kinetics was followed on a Hitachi 200-10 spectrophotometer combined with a QD 15 recorder. Reactions were run under pseudo first order conditions with Zn^{2+} and Co^{2+} in excess, typically 10^{-4} to 10^{-2} *M* and the complex in the range 10^{-5} *M*. The formation of the Zn(II) and the Co(II) porphyrin complex was followed directly by measuring the increase in absorbance at the 406 and 395 nm, the respective peak wavelengths of the formed complex. It is also possible to follow the decrease in absorbance at the 418 nm peak of the Mn(II)P. The Mn(II)P decomposes slowly, the rate is larger at lower pHs. the largest first order rate constant for the self decay of Mn(II)P is about 2 X 10^{-6} S^{-1}.

Most of the kinetic runs were done with 1*M* NH_4Cl and adjusting the pH (6.5 to 8) of the solution before the dithionite was added. The ammonium chloride provided the source of ammonia in solution. The total free ammonia in the solution was determined using the value of $-\log K_{NH_4^+}$ at 25 °C as 9.48 [6]. The temperature control (0.1°) of the reaction solution was provided by the thermostated water circulated in the metal jacket surrounding the cell.

Results and Discussion

Mn(II)P–Zn^{2+} Reaction

First order plots were obtained under pseudo first order conditions used for the experiments. Plots of the variation of the first order rate constants with the total concentration of zinc are given in Fig. 2. All the lines pass through the origin. The slope of the line gives the second order rate constant for each pH.

The rate of the reverse reaction is very slow and is neglected. However, it should be mentioned that the Mn(II)P in the equilibrated solution, on preserving for a few hours, slowly gets converted to the Mn(III) complex.

The second order rate constants are pH dependent. The value decreases with increase in pH, as is seen from Table I. The variation is not a simple pH effect, but is dependent on the amount of free ammonia [6] in solution was verified by varying the NH_4Cl concentration at constant pH. On the other hand the variation of the NH_4^+ concentration for constant free ammonia had but little effect on the k_{obs}. Fig. 3 gives the plot of the k_{obs} *vs.* NH_3 concentration at 25 °C. Each experimental point in the graph is obtained from the slope of the k_1 *vs.* total zinc concentration plots. The error in each of the rate constants is within 5%. Addition of excess Mn^{2+} (the displaced ion to the system) had no effect

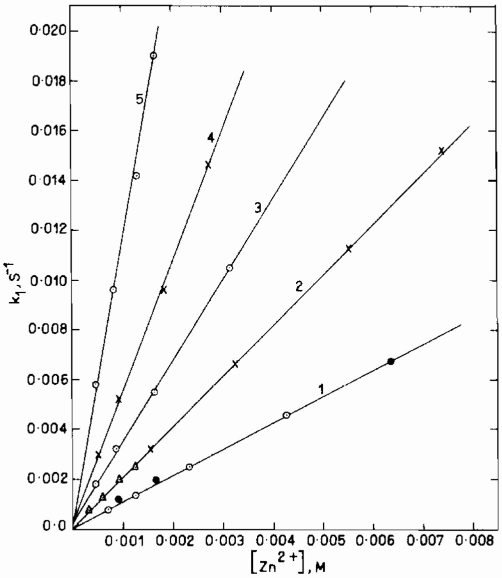

Fig. 2. Zinc dependence of the first order rate constants of the exchange with the manganese(II) porphyrin. Ammonia concentrations are (1) 1650 X 10^{-5} *M* (temp. 25 °C); (2) 1160 X 10^{-5} *M* (temp. 25 °C); (3) 850 X 10^{-5} *M* (temp. 25 °C); (4) 850 X 10^{-5} *M* (temp. 34.5 °C); (5) 770 X 10^{-5} *M* (temp. 40 °C).

TABLE I. Rate Constants for Manganese(II) Porphyrin Exchange Reaction with Zinc. Temp. = 25 °C.

$[NH_4^+]$ *M*	pH	$[NH_3] \times 10^5$ *M*	$[Mn^{2+}]$ *M*	k_{obs}* M^{-1} S^{-1}
1.06	7.10	440	0	6.30
1.06	7.25	620	0	5.75
1.06	7.32	731	0	3.68
1.06	7.50	1140	0	2.50
1.06	7.70	1752	0	0.77
2.0	7.25	1174	0	2.30
1.13	7.45	1050	0	2.67
1.33	7.65	1980	0	0.61
2.00	7.40	1650	0	0.86
0.24	6.50	25.0	0	4.97
0.24	6.90	62.5	0	8.17
0.24	7.40	198.0	0	9.97
0.24	8.0	792.0	0	4.48
0.24	8.15	1116	0	2.98
1.13	7.45	1050	0.0125	2.67
1.13	7.45	1050	0.0375	2.67
2.0	7.40	1650	0.0125	0.86
2.0	7.40	1650	0.050	0.86

*The second order rate constant k_{obs} was obtained for each condition from the slope of first order rate constants against zinc concentration, the reaction run under pseudo first order condition. Error within 5%.

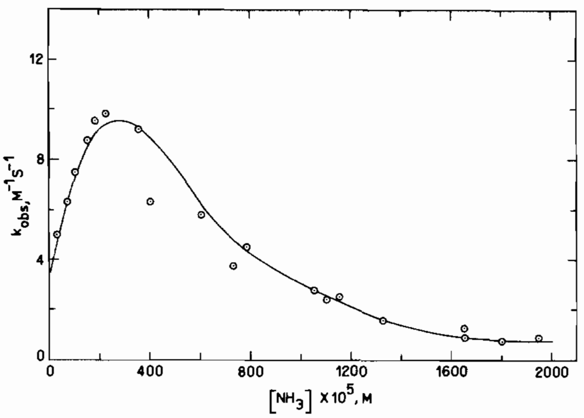

Fig. 3. Ammonia dependence of the observed second order rate constants of the exchange reaction of Mn(II) porphyrin with zinc at 25 °C. Each point in the graph is determined from the slope of the plots as given in Fig. 2. The circles give the experimental points and the solid line is drawn based on eqn. 2 using the rate constants and equilibrium constants as given in the text.

on the k_{obs} (see Table I). This argues against the possibility of a predissociation mechanism for the exchange.

Analysis of the k_{obs} with the change in NH_3 concentration showed that only the Zn^{2+} and the $Zn{-}NH_3^{2+}$ species are contributing to the displacement. At higher concentrations of NH_3, the higher ammino complexes of Zn are also formed in appreciable amounts. This decreases the effective concentration of the Zn^{2+} and $Zn{-}NH_3^{2+}$ in solution, thus influencing the k_{obs}. The concentrations of Zn^{2+} and $Zn{-}NH_3^{2+}$ for a particular condition were calculated from the expression

$$Zn_T = Zn^{2+}(1 + K_1[NH_3] + K_1K_2[NH_3]^2 + + K_1K_2K_3[NH_3]^3 + K_1K_2K_3K_4[NH_3]^4) \quad (1)$$

where K_1, K_2 *etc.* are the stepwise formation constants [7] of the zinc–ammine complexes. Thus

$$k_{obs}[Zn_T] = k_I[Zn^{2+}] + k_{II}[Zn{\cdot}NH_3^{2+}] \quad (2)$$

The values of k_I and k_{II} which give the best experimental fit are 3.3 M^{-1} S^{-1} and 33.0 M^{-1} S^{-1} respectively. The smooth curve in Fig. 3 is the second order rate constants computed for various NH_3 concentrations using values of k_I and k_{II}. The deviation is large when larger concentrations of NH_4^+ were employed in the kinetic run. This is attributed to the large error which arises in the NH_3 concentrations for small pH differences, the latter being the directly measured value.

In order to determine the activation parameters, kinetic experiments were performed in the range 25 to 45 °C for different regions of Fig. 3 at varying pH. Some typical values are given in Table II. The activation energies obtained for the three regions are the same and equal to 9.5 kcal/mol. This indicates the existence of a pre-equilibrium having favourable entropy of the order of –28 e.u. and –21 e.u. respectively for the two zinc ion species reacting with Mn(II)P.

TABLE II. Rate Constants for Manganese(II) Porphyrin Exchange Reaction with Zinc at Different Temperatures and Different Ammonia Concentrations.

Temp.	$k_{obs} M^{-1} S^{-1a}$	$k_{obs} M^{-1} S^{-1b}$	$k_{obs} M^{-1} S^{-1c}$
24.5	3.77	5.06	–
25.5	–	–	5.83
32.0	4.40	6.60	–
38.0	6.02	7.76	9.50
40.0	–	–	11.10
45.0	8.82	11.0	–

$^a[NH_3] = 950 \times 10^{-5} M$. $^b[NH_3] = 612 \times 10^{-5} M$.
$^c[NH_3] = 510 \times 10^{-5} M$.

TABLE III. Rate Constants for the Incorporation of Zinc into the Porphyrin in Ammoniacal Environments. Temp. = 25 °C.

$[NH_4^+]$ *M*	pH	$[NH_3] \times 10^5$ *M*	$k_{obs}, M^{-1} S^{-1}$
0.266	6.7	46.7	3.85
0.266	6.8	58.0	4.62
0.266	7.3	185	7.00
0.266	7.8	582	6.92
1.087	6.1	44.0	3.28
1.087	6.9	260	7.50
1.087	7.4	920	1.67
1.087	7.7	1900	0.50
2.00	7.4	1650	1.00
1.14	4.9	–	0.67
1.14	5.2	–	1.35
1.14	5.9	–	1.43
0	5.2	–	0.25

In order to confirm the finding that the dependence of rate of exchange on the ammonia concentration arises from the different displacing ion and is not due to changes in the Mn(II)P complex, experiments were performed on the incorporation of zinc into the free porphyrin in the ammoniacal environments. The results are summarized in Table III. The dependence of the rate constants on the ammonia concentration is very similar to that of the reaction with Mn(II)P although the actual rate constants under identical conditions are slightly less [k_I = 1.67 M^{-1} S^{-1} and k_{II} = 25 M^{-1} S^{-1}]. A similar increase in rate was observed recently by Hambright *et al.* [8] for the displacement reaction of cadmium porphyrins with Zn^{2+} compared to the zinc incorporation into the same porphyrins. It should be noted that the incorporation and the displacement capacity of the $Zn-NH_3^{2+}$ species is nearly ten fold greater than that of the Zn^{2+}. The ammoniacal environment enables the determination of the rate constant for the reaction of Zn^{2+} with the neutral porphyrin species. In the earlier studies [9, 10] of the zinc incorporation into this porphyrin in acid conditions, the contribution from the protonated species was considerable. The present study showed also that even in acid pHs the NH_4^+ influences the zinc incorporation into the porphyrin. A value of $k_{obs} = 1.4\ M^{-1}\ S^{-1}$ was observed at a pH of 5.2 and NH_4^+ *1.0 M* compared to 0.25 $M^{-1}\ S^{-1}$ at the same pH with no NH_4^+ present.

Mn(II)P–Co^{2+} Reaction

Cobalt in ammoniacal medium exchanges the ligand from Mn(II)P to give the Co(II)P and which subsequently changes to the Co(III)P slowly. The spectra of Co(III)P and Co(II)P in ammoniacal environments are also given in Fig. 1. The reaction order is similar to the zinc displacement. As seen in Fig. 4, straight line plots were obtained when the pseudo first order rate constants were plotted against the total concentration of cobalt. Unlike the zinc reaction, such plots give a finite value of the intercept and the intercepts increase with increase in pH. Because of this, it became essential that the second order rate constants were always determined from the slope of such plots for all the pHs studied. The rate constants are summarized in Table IV. The rate constants increase and tend to reach a limiting value for the pH range studied. For the ammonia concentrations we have studied, the main species of cobalt are Co^{2+}, $Co-NH_3^{2+}$, $Co-(NH_3)_2^{2+}$ and $Co-(NH_3)_3^{2+}$. Analysis of the rate constants showed that the $Co-(NH_3)_2^{2+}$ species also contribute to the overall rate of the reaction and that of Co^{2+} is negligible. The rate constants k_{II} and k_{III} for the reaction of the mono and diammine-cobalt complex, with Mn(II)P, calculated are 1.16 $M^{-1}\ S^{-1}$ and 0.67 $M^{-1}\ S^{-1}$ respectively.

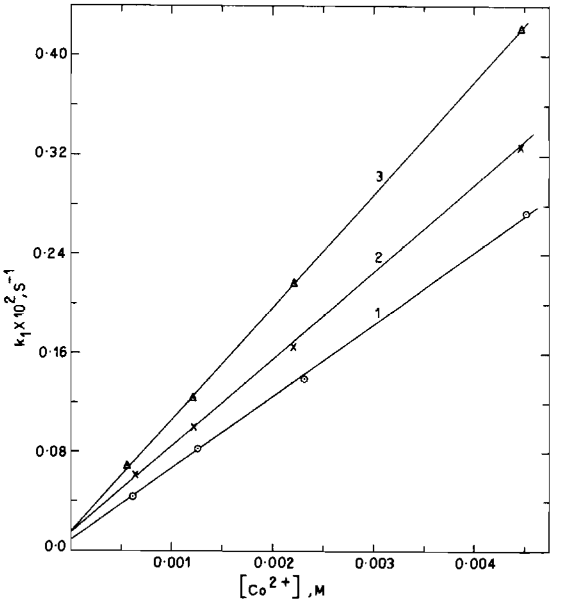

Fig. 4. Plots of the first order rate constants against the concentration of cobalt at different ammonia concentrations for the exchange reaction of manganese(II) porphyrin with cobalt at 25 °C. (1) $[NH_3] = 528 \times 10^{-5}$ *M*; (2) $[NH_3] = 1040 \times 10^{-5}$ *M*; (3) $[NH_3] = 2090 \times 10^{-5}$ *M*.

TABLE IV. Rate Data for Manganese(II) Porphyrin Exchange Reaction with Cobalt in Ammoniacal Environments. Temp. = 25 °C.

$[NH_3] \times 10^5, M$	$k_{obs}\ M^{-1}\ S^{-1}$
165	0.25
522	0.53
528	0.53
737	0.60
930	0.63
1056	0.73
1479	0.87
2090	0.93

Direct insertion reaction of Co^{2+} with the porphyrin could not be performed for comparative studies. The reaction is quite slow compared to the zinc insertion and the final product is the Co(III)P [11]. Also, we observed that on preserving, the equilibrated solution of $Mn(II)P-Co^{2+}$ system, the Co(II)P is partly converted to the Co(III)P and partly decomposed.

The order of the ratio of the rate constants of the $Zn-NH_3^{2+}$ to $Co-NH_3^{2+}$ is in the same range as that of the insertion reaction of these ions to ligands like dimethyl amino phenyl azopyridine and terpyridines [12].

It is difficult to speculate the reason for the nonreactivity of the Co^{2+} species with the Mn(II)P. Both penta and hexa coordinated cobalt porphyrins are known [13] and hence the reactivity of the $Co-NH_3^{2+}$ and $Co-(NH_3)_2^{2+}$ in the displacement are understood. However, zinc porphyrin is known [13] to add only one extra ligand and this argues for the reactivity of $Zn-NH_3^{2+}$ but not the $Zn-(NH_3)_2^{2+}$ species. The ten fold increase in the rate constant for the incorporation of $Zn-NH_3^{2+}$ compared to Zn^{2+} can be compared with results of copper incorporation into the mesoporphyrin in presence of oxine, where maximum rate is observed for the 1:1 complex of copper–oxine [14].

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References

1 P A Loach and M Calvin, *Biochem*, *2*, 361 (1963)
2 L J Boucher, *Coord Chem Rev*, *7*, 289 (1972)
3 R R Das and B S Prabhananda, *J Inorg Nucl Chem*, *41*, 1615 (1979)
4 R R Das and K N Rao, *'Proceedings of the 20th International Conf Coord Chem', Calcutta*, India, Dec 1979, p 305
5 R R Das and R A Plane, *J Inorg Nucl Chem*, *37*, 147 (1975)
6 D H Everett and D A Landsman, *Trans Faraday Soc*, *50*, 1221 (1954)
7 L G Sillen, Stability Constants of Metal-ion Complexes Part I Inorganic Ligands The Chem Soc London (1971)
8 J Reid and P Hambright, *Inorg Chim Acta*, *33*, L135 (1979)
9 T P Stein and R A Plane, *J Am Chem Soc*, *91*, 607 (1969)
10 R R Das, *J Inorg Nucl Chem*, *34*, 1263 (1972)
11 R F Pasternack and M A Cobb, *J Inorg Nucl Chem*, *35*, 4327 (1973)
12 L I Budarin and K B Yatsimirskii, *Russ Chem Rev*, *37*, 209 (1968)
13 J E Falk, 'Porphyrins and Metalloporphyrins', Elsevier, N Y (1964) p 41
14 M B Lowe and J N Phillips, *Nature*, *190*, 262 (1961)