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Preliminary Communication

Kinetic Study of the Substitution of Pyridine by Cyanide in the bis(pyridine)cobalt(III)hematoporphyrin-IX: Distinguishing between the I_d and D Mechanism

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A kinetic study of the reaction between the cyanide ion and the bis(pyridine)cobalt(III)hematoporphyrin-IX complex to give $(CN)_2$cobalt(III)hematoporphyrin-IX has shown that the axial ligand substitution occurs by a purely dissociative (D but not I_d) mechanism in chloroform involving predissociation to a five-co-ordinate (pyridine)cobalt(III)hematoporphyrin-IX complex.

A dissociative mechanism has been advanced for most of the metalloporphyrin substitution reactions.[1,2] It is surprising that »mass-law (rate) retardation« in nonco-ordinating solvents has been utilized only to a minor extent for differentiation between closely related I_d and D mechanisms.[3,4] Our kinetic studies of the reaction of the cyanide ion with $(py)_2$Co(hemato-IX) (py = pyridine, hemato-IX = hematoporphyrin-IX) in chloroform eliminate the possibility of the I_d process and provide strong support for the D mechanism.** The stoicheiometry of the over-all reaction was found spectrophotometrically to be:

$$(py)_2Co(hemato\text{-}IX) + 2\,CN^- = (CN)_2Co(hemato\text{-}IX) + 2\,py \qquad (1)$$

where the reactant and product were identified by their visible absorption spectrum[5].

Reaction (1) proceeds to completion under the conditions employed in this study. The kinetics were studied spectrophotometrically by monitoring the change in the Soret region at 25 °C in chloroform containing less than 0.01 M $[H_2O]$ and under pseudo-first-order conditions. Our kinetic data show an inverse dependence on pyridine and between the first- and zero-order in cyanide ion concentration. This observation supports the previous statement that the second axial anion incorporation is rapid.[1,2,6] The data presented are in full agreement with the dissociative mechanism depicted by equation (2).

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** The over-all charge on the metalloporphyrin molecule is not shown throughout the paper.

$$\left.\begin{array}{l} (\mathrm{py})_2\mathrm{Co(hemato\text{-}IX)} \underset{+\,\mathrm{py},\ k_{-1}}{\overset{-\mathrm{py},\ k_1}{\rightleftharpoons}} (\mathrm{py})\mathrm{Co(hemato\text{-}IX)} \\ (\mathrm{py})\mathrm{Co(hemato\text{-}IX)} \xrightarrow{+\mathrm{CN}^-,\ k_2} (\mathrm{py})(\mathrm{CN})\mathrm{Co(hemato\text{-}IX)} \\ (\mathrm{py})(\mathrm{CN})\mathrm{Co(hemato\text{-}IX)} \xrightarrow[\text{fast}]{-\mathrm{py},\ +\,\mathrm{CN}^-} (\mathrm{CN})_2\mathrm{Co(hemato\text{-}IX)} \end{array}\right\} \qquad (2)$$

The rate law, assuming a steady state for the five-co-ordinate intermediate (py)Co(hemato-IX) is

$$\text{rate} = \frac{k_1\,[(\mathrm{py})_2\mathrm{Co(hemato\text{-}IX)}]}{(k_{-1}/k_2)\,([\mathrm{py}]/[\mathrm{CN}^-]) + 1} = k_{\mathrm{obs}}\,[(\mathrm{py})_2\mathrm{Co(hemato\text{-}IX)}] \qquad (3)$$

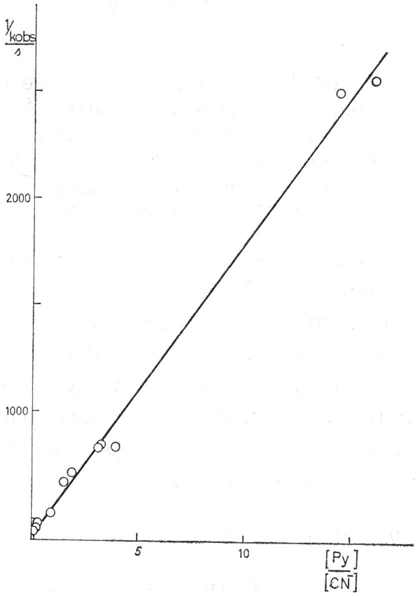

Figure $(k_{\mathrm{obs}})^{-1}$ *vs.* concentration ratio [pyridine]/[CN^-] for reaction (1).

The plot of $(k_{\mathrm{obs}})^{-1}$ *versus* [py]/[CN^-] gives a straight line with a nonzero intercept and yield the k_{-1}/k_2 and k_1 values of 0.35 and $2.50 \times 10^{-3}\ \mathrm{s}^{-1}$, respectively.

An obvious variant of this mechanism, which is kinetically indistinguishable from that shown above, is the one which involves formation of the intermediate aquo-complex *via* the $\mathrm{I_d}$ mechanism, since the solvent chloroform may contain as much as 0.01 M [$\mathrm{H_2O}$]. The application of the steady state condition to the intermediate aquo-complex leads to a rate law identical in form with equation (3), but it can be ruled out on the basis of the fact that the controlled varying water amount in chloroform does not influence the rate of axial substitution as shown in the Table. This conclusion is unsafe if the cation-dipol association constant between the substrate and water molecule is very high.

The extension of this method to other bis-ligated metalloporphyrins is in progress.

TABLE

Rate Data for the Reaction (2)

[py]/mol l^{-1}	[CN$^-$]^a/mol l^{-1}	k_{obs}/s^{-1}	k_{-1}/k_2
0	0.08	2.7×10^{-3}	
0	0.02	2.1×10^{-3}	
0	0.005	2.4×10^{-3}	
0	0.004	2.5×10^{-3}	
0	0.004	2.4×10^{-3b}	
0	4×10^{-4}	2.7×10^{-3}	
4×10^{-3}	2.5×10^{-4}	3.9×10^{-4}	0.34
8×10^{-4}	2.5×10^{-4}	1.2×10^{-3}	0.34
4×10^{-4}	2.5×10^{-4}	1.5×10^{-3}	0.37
5×10^{-4}	1.4×10^{-3}	2.2×10^{-3}	0.37
0.001	5×10^{-3}	2.3×10^{-3}	0.44
0.001	2.5×10^{-3}	2.1×10^{-3}	0.33
0.001	1×10^{-3}	1.9×10^{-3}	0.34
0.001	5×10^{-4}	1.4×10^{-3}	0.37
0.001	3×10^{-4}	1.2×10^{-3}	0.32
0.001	2.5×10^{-4}	1.2×10^{-3}	0.32
0.001	7×10^{-5}	4×10^{-4}	0.36
0.001	7×10^{-5}	4×10^{-4}	0.36^c
0.001	5×10^{-4}	1.4×10^{-3}	0.37^c
0	5×10^{-4}	2.4×10^{-3c}	

[a] Added as tetrabutylammonium-cyanide.

[b] The starting concentration of bis(pyridine)cobalt(III)hematoporphyrin-IX acetate was 2.7×10^{-5} M. In all the other runs it was 7×10^{-6} M.

[c] Chloroform was dried by freshly prepared BDH A 4 molecular sieves lowering the water content from 0.01 M to less than 0.002 M [H_2O].

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SAŽETAK

Kinetičko ispitivanje supstitucije piridina sa cijanidom u bis(piridin)kobalt(III)hematoporfirin-IX: Razlikovanje I_d i D mehanizama

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Kinetičko ispitivanje reakcije cijanid-iona s bis(piridin)kobalt(III)hematoporfirin-IX kompleksom u kloroformu, pri čemu kao reakcijski produkt nastaje bis(cijanido)kobalt(III)hematoporfirin-IX kompleks, pokazuje da supstitucija aksijalno vezanih liganada slijedi čisti disocijacijski (D a ne I_d) mehanizam koji predviđa stvaranje (piridin)kobalt(III)hematoporfirin-IX pentakoordiniranog međuprodukta.

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