Electron Exchange Rates of Cobalt Tetra-arylporphines

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Summary The first accurate direct measurements of electron exchange rates of cobalt(III)–cobalt(II) tetraphenylporphyrins indicate rate constants of 9·69 dm^3 mol^{-1} s^{-1} [outer-sphere for bis(pyridine) complexes] and 2·71 × 10^4 dm^3 mol^{-1} s^{-1} (chloride-bridged inner-sphere) in $CDCl_3$.

The electron-transfer behaviour of metalloporphyrins has recently received great interest owing to their modelling of the biological electron-transfer metalloproteins such as the cytochromes.[1–4] Traditionally, measurements of electron self-exchange rates of metalloporphyrins have been estimated from Marcus theory treatments, *i.e.*, from cross-reaction rates with small inorganic reductants. Since such treatments offer only theoretical predictions of the unknown exchange rates, which in some cases (particularly some involving cobalt complexes) have shown rather large deviations from actual, measured rates,[5] a convenient method by which such rates could be directly measured was desired and is described here.

The method was developed with experiments involving electron exchange between cobalt(III) and cobalt(II) complexes of tetra-arylporphines. Outer-sphere exchange rates were measured by allowing 5,10,15,20-tetraphenylporphinatocobalt(III) ($Co^{III}TPP$) to react with the methyl-labelled 5,10,15,20-tetra(*p*-tolyl)porphinatocobalt(II) [$Co^{II}TTP$] in the presence of C_5D_5N in $CDCl_3$. The exchange reaction (1) is observed and the progress of the reaction is monitored by the appearance of $Co^{III}TTP$ through the *p*-methyl peak of its ^{1}H n.m.r. spectrum (in a series of consecutive spectra taken after mixing) as a function of time. Such observation is possible because of the downfield isotropic shifts of $Co^{II}TTP$'s ^{1}H n.m.r. spectrum.[6] Thus, the diamagnetic bis(pyridine) complex of $Co^{III}TTP$, $Co^{III}TTP(py)_2{}^+Cl^-$, formed by dissolution of $Co^{III}TTP(Cl)$ in C_5D_5N–$CDCl_3$ solutions, shows its *p*-methyl resonance at δ 2·63 from Me_4Si, while that of paramagnetic $Co^{II}TTP$ occurs at δ *ca.* 3·5—4·1, depending on the presence of other ligands in solution.

$$\mathrm{Co^{III}TPP + Co^{II}TTP = Co^{II}TPP + Co^{III}TTP} \qquad (1)$$

To account for the extent of the various complexes present, owing to co-ordination of C_5D_5N to the original porphyrins, the relevant equilibrium constants of complexation were also measured for the systems under consideration, equations (2) and (3). K_1 and K_2 were measured by visible spectrophotometric titrations,[7] which indicated values of $K_1 = 478 \pm 67$ dm^3 mol^{-1} and $K_2 = 0{\cdot}110 \pm 0{\cdot}043$ dm^3 mol^{-1} at 25·5 °C. The mono(pyridine) and bis(pyridine) complexes of $Co^{III}TPP$ show slightly different chemical shifts of the β-pyrrole peaks in their ^{1}H n.m.r. spectra.[8]

$$\mathrm{Co^{II}TTP} \overset{\substack{\mathrm{py}\\(K_1)}}{\rightleftharpoons} \mathrm{Co^{II}TTP(py)} \overset{\substack{\mathrm{py}\\(K_2)}}{\rightleftharpoons} \mathrm{Co^{II}TTP(py)_2} \qquad (2)$$

$$\mathrm{Co^{III}TPP(Cl)} \overset{\substack{\mathrm{py}\\(K_3)}}{\rightleftharpoons} \mathrm{Co^{III}TPP(py)^+Cl^-} \overset{\substack{\mathrm{py}\\(K_4)}}{\rightleftharpoons} \mathrm{Co^{III}TPP(py)_2{}^+Cl^-} \qquad (3)$$

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Thus, the peaks appear at $\delta_{\mathrm{mono(L)}}$ 8·98 and $\delta_{\mathrm{bis(L)}}$ 9·09; so relative amounts of the two species were determined from ^{1}H n.m.r. spectra of solutions of low C_5D_5N concentration. These constants were determined to be $K_3 = 10^{4 \cdot 98 \pm 0 \cdot 11}$ and $K_4 = 10^{3 \cdot 62 \pm 0 \cdot 09}$ at 27·7 °C. From visible spectra, co-ordination by pyridine has been seen to occur on a time-scale of <1 min even at cobalt porphyrin concentrations 10^3 times lower and pyridine concentrations 10 times lower than those used for the exchange reactions and the determinations of K_3 and K_4 here.

In solutions of $[\mathrm{py}]_{\mathrm{total}} \geqslant$ *ca.* 0·01 M, as used for the outer-sphere experiments, $\mathrm{Co^{III}TPP(py)_2{}^+Cl^-}$ is the predominant $\mathrm{Co^{III}}$ species, owing to its high overall formation constant, but several $\mathrm{Co^{II}}$ porphyrins exist simultaneously and the observed rate of exchange has contributions from exchange with each $\mathrm{Co^{II}}$ species [equations (4) and (5)]

$$V_{\mathrm{exch}} = (k_{11})_{\mathrm{obsd}}[\mathrm{Co^{II}}]_{\mathrm{total}}[\mathrm{Co^{III}}]_{\mathrm{total}} \quad (4)$$

$$= k_0[\mathrm{Co^{II}}][\mathrm{Co^{III}}]_{\mathrm{t}} + k_1[\mathrm{Co^{II}(py)}][\mathrm{Co^{III}}]_{\mathrm{t}} + k_2[\mathrm{Co^{II}(py)_2}][\mathrm{Co^{III}}]_{\mathrm{t}} \quad (5)$$

where the presence of the porphyrin ligand is assumed in each complex. Knowledge of the equilibrium constants of co-ordination and, therefore, the concentration of each exchanging species, allows resolution of the observed rate constant into its components from a pyridine concentration dependence study. Rate constants at 27·7 °C in $\mathrm{CDCl_3}$ were determined as $[\mathrm{Co^{III}TPP(py)_2{}^+Cl^-} + \mathrm{Co^{II}TTP}]$ $k_0 = 0{\cdot}0191$, $[\mathrm{Co^{III}TPP(py)_2{}^+Cl^-} + \mathrm{Co^{II}TTP(py)}]$ $k_1 = 0{\cdot}129$, and $[\mathrm{Co^{III}TPP(py)_2{}^+Cl^-} + \mathrm{Co^{II}TTP(py)_2}]$ $k_2 = 9{\cdot}69$ dm^3 mol^{-1} s^{-1}. As determined from a temperature dependence study, observed activation parameters at 0·070 M total C_5D_5N are $\Delta H^{\ddagger} = 8{\cdot}4 \pm 1{\cdot}9$ kcal/mol and $\Delta S^{\ddagger} = -34 \pm 6$ cal mol^{-1} K^{-1}.

Inner-sphere exchanges were also studied using $\mathrm{Co^{III}TTP}$ complexes which retain their co-ordinated anion in the absence of added ligand. These exchanges of the CoTTP complexes are fast enough to cause extensive broadening of the ^{1}H n.m.r. spectra. The effect of various bridging ligands was studied, and most rates were determined at the temperatures of coalescence of the *p*-methyl peaks in several solutions of varying concentrations, yielding rate constants and activation parameters for exchange.[9] For the chloride-bridged exchange, these are $k_{11}(298\ \mathrm{K}) = 2{\cdot}71 \times 10^4$ dm^3 mol^{-1} s^{-1}, $\Delta H^{\ddagger} = 10{\cdot}3 \pm 1{\cdot}5$ kcal/mol, $\Delta S^{\ddagger} = -3{\cdot}6 \pm 4{\cdot}7$ cal mol^{-1} K^{-1}. The order of bridging efficiencies found is $\mathrm{I^-} > \mathrm{N_3{}^-} \simeq \mathrm{SCN^-} > \mathrm{Br^-} > \mathrm{Cl^-}$. A solvent dependence study of the chloride-bridged exchange showed relative rates in C_6D_6, $\mathrm{CDCl_3}$, and [$^2H_8$]tetrahydrofuran in the ratios of 18 : 1 : 0·1. The catalysis by several orders of magnitude through mediation of the anion is similar to results reported by Durham *et al.*[10] for other macrocyclic cobalt complexes.

Thus, a few relatively simple experiments can afford a large amount of information useful in general electron transfer behaviour of these metalloporphyrin model systems and could be extended to corroborate the previous predictions of cobalt porphyrin self-exchange rates.[2,4]

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