Kinetics of Binding of Imidazole to αβγδ-Tetraphenylporphinatoiron(III) in Dimethyl Sulphoxide

By Robert F. Pasternack* and James R. Stahlbush
(*Department of Chemistry, Ithaca College, Ithaca, New York* 14850)

Summary A mechanism is proposed for the complexation of αβγδ-tetraphenylporphinatoiron(III) by imidazole in dimethyl sulphoxide in which the substitution of the second imidazole ligand for a bound solvent molecule is rate determining.

Interpretations of previous studies of the kinetics of bonding of ligand molecules to iron porphyrins have had to contend with complications such as mixed solvents,[1] multiple forms of the attacking ligand and metalloporphyrin,[1,2] and the necessity of using micelles to solvate the porphyrin to prevent aggregation.[3] In the present study these complications are avoided by considering the interaction of $\alpha\beta\gamma\delta$-tetraphenylporphinatoiron(III) chloride (FeTPPCl) and imidazole (Im) in the polar, aprotic solvent Me_2SO.

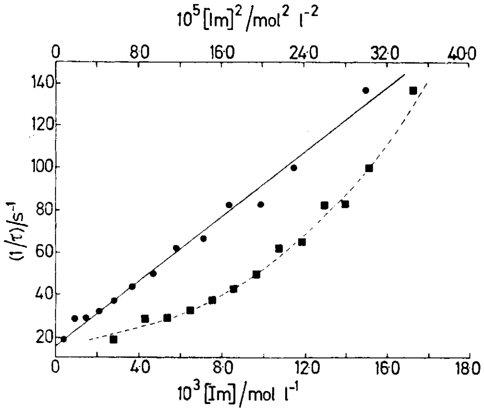

FIGURE. Plot of τ^{-1} *vs.* $[Im]^2$ (●) and *vs.* $[Im]$ (■) at 25 °C, $\mu = 0{\cdot}040\ mol\ l^{-1}$. The parabolic nature of the latter plot indicates that the kinetics have been studied over a sufficiently wide concentration range unambiguously to determine the order of the reaction with respect to imidazole.

FeTPPCl was synthesized according to literature methods.[4] The substantial difference between the spectrum of FeTPPCl in Me_2SO and spectra obtained in nonco-ordinating solvents[5] indicates that the major metalloporphyrin species in solution is $FeTPP(Me_2SO)^+$ rather than FeTPPCl. Magnetic susceptibility measurements obtained using Evans' method[6] indicate that the iron atom in $FeTPP^+$ is high-spin and hence five-co-ordinate[7] in Me_2SO and is low-spin and six-co-ordinate in the presence of a large excess of imidazole. A spectrophotometric titration revealed that there are at most two absorbing species in solution, $FeTPP(Me_2SO)^+$ and $FeTPP(Im)_2$. The equilibrium constant for reaction (1) is $6.3 \times 10^4\ l^2\ mol^{-2}$ at

$$FeTPP(Me_2SO)^+ + 2Im \underset{k_r}{\overset{k_f}{\rightleftharpoons}} FeTPP(Im)_2^+ + Me_2SO \qquad (1)$$

25 °C and at an ionic strength of $0{\cdot}040\ mol\ l^{-1}$ in $NaNO_3$. The equilibrium constant was shown to be almost invariant with respect to ionic strength below μ *ca.* $0{\cdot}05\ mol\ l^{-1}$.

The kinetics of the complexation reaction (1) were studied using the temperature-jump technique under the conditions: $[FeTPP^+] = 1{\cdot}27 \times 10^{-4}\ mol\ l^{-1}$, $2{\cdot}81 \times 10^{-3} \leqslant [Im] \leqslant 1{\cdot}73 \times 10^{-2}\ mol\ l^{-1}$, $\mu = 0{\cdot}040\ mol\ l^{-1}$, $t = 25$ °C. The wavelength of observation was 526 nm. A plot of τ^{-1} against $[Im]^2$ is linear (Figure). We obtain $k_f = 3{\cdot}8 \pm 0{\cdot}4 \times 10^5\ l^2\ mol^{-2}\ s^{-1}$ and $k_r = 17 \pm 2\ s^{-1}$.

A two-step mechanism consistent with the experimental results is shown in equations (2) and (3). The first step is

$$FeTPP(Me_2SO)^+ + Im \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeTPP(Me_2SO)(Im)^+ \qquad (2)$$

$$FeTPP(Me_2SO)(Im)^+ + Im \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} FeTPP(Im)_2^+ + Me_2SO \qquad (3)$$

the addition of an imidazole molecule to the distal side of the solvated porphyrin. The iron atom may (but need not necessarily) change in this step from high-spin to low-spin;[8] previous studies have shown that such a change in spin state can be very rapid.[9] The second step involves the substitution of an imidazole molecule for a solvent molecule, a step, which in analogy to other metalloporphyrin substitution reactions, we believe to be primarily S_N1 in character.[10] Equation (4) gives an expression for τ^{-1} resulting from this mechanism, utilizing the steady-state approximation for $FeTPP(Me_2SO)(Im)^+$ and the experimental fact that $[Im]_{total} >> [FeTPP^+]_{total}$. When

$$\tau^{-1} = (k_1k_2[Im]^2 + k_{-1}k_{-2})/(k_{-1} + k_2[Im]) \qquad (4)$$

$k_{-1} >> k_2[Im]$, equation (4) reduces to equation (5) and k_f is given by equation (6). The rates of breaking of $FeTPP^+$–solvent bonds have been determined[11] in dimethylformamide and MeOH as $> 10^6\ s^{-1}$. If this approximate value is applicable here, K_1, the stability constant for the

$$\tau^{-1} = (k_1k_2/k_{-1})[Im]^2 + k_{-2} \qquad (5)$$

$$k_f = k_1k_2/k_{-1} = K_1k_2 \text{ while } k_r = k_{-2} \qquad (6)$$

formation of $FeTPP(Me_2SO)(Im)^+$, will be less than unity. This result is consistent with the lack of appreciable build-up of the monoimidazole adduct in solution.

We thank the National Institutes of Health and the Petroleum Research Fund for support of this research. We also acknowledge useful discussions with Dr. Glenn C. Vogel of this department.

(*Received*, 16*th August* 1976; *Com.* 940.)

---

[1] B. B. Hasinoff, H. B. Dunford, and D. G. Horne, *Canad. J. Chem.*, 1969, **5**, 3225.

[2] G. B. Kolski and R. A. Plane, *J. Amer. Chem. Soc.*, 1972, **94**, 3740.

[3] J. Simplicio, *Biochem.*, 1972, **11**, 2529; P. Hambright and P. B. Chock, *J. Inorg. Nuclear Chem.*, 1975, **37**, 2363.

[4] A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476; A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2443.

[5] P. R. Ciaccio, J. V. Ellis, M. E. Munson, G. L. Kedderis, F. X. McConville, and J. M. Duclos, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1885.

[6] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

[7] J. L. Hoard, *Science*, 1971, **174**, 1295.

[8] The spin state of mixed ligand–solvent adducts of iron porphyrins remains uncertain although monocyanohemin has been recently reported as being low-spin in Me_2SO (J. T. Wang, H. J. C. Yeh, and D. F. Johnson, *J. Amer. Chem. Soc.*, 1975, **96**, 1968).

[9] J. K. Beattie, N. Sutin, D. H. Turner, and G. W. Flynn, *J. Amer. Chem. Soc.*, 1973, **95**, 2052.

[10] N. S. Angerman, B. B. Hasinoff, H. B. Dunford, and R. B. Jordan, *Canad. J. Chem.*, 1969, **47**, 3217; R. F. Pasternack, M. A. Cobb, and N. Sutin, *Inorg. Chem.*, 1975, **14**, 866.

[11] J. Hodgkinson and R. B. Jordan, *J. Amer. Chem. Soc.*, 1973, **95**, 763.