Inorganica Chimica Acta,

Reaction of N-Substituted Imidazoles with Ferrous Phthalocyanine in Dimethylsulphoxide

J. G. JONES[a] and M. V. TWIGG[b]

University Chemical Laboratory, Canterbury (U.K.)

(Received November 20, 1974)

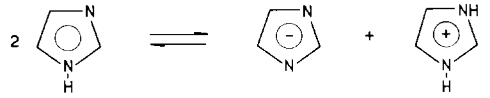
Previously, we have shown that in dimethylsulphoxide (dmso) ferrous phthalocyanine (FePc) reacts with imidazole to form a bis-imidazole complex at conveniently measurable rates.[1] When dissolved in dmso, square planar FePc most probably exists as FePc(dmso)$_2$, with two solvent molecules bound to the metal centre.[2] Displacement of the first solvent molecule is rate determining:

$$\mathrm{FePc(dmso)_2} \xrightarrow{\text{slow}} \mathrm{FePc(dmso)(imid)} \xrightarrow{\text{fast}} \mathrm{FePc(imid)_2}$$

and at a given temperature, observed pseudo first order rate constants are given by the equation

$$k_{\mathrm{obs}} = k[\mathrm{imid}]$$

This may be interpreted in terms of an associative or limiting dissociative mechanism.[1] However, no evidence for the latter could be obtained.[3] It is possible that the mechanism is associative and involves the highly nucleophilic imidazolate anion, rather than imidazole itself:



Although we were unable to obtain direct evidence for this equilibrium from conductivity measurements (imidazole behaves as a non-electrolyte in dmso at 25 °C) this does not completely rule out the possible involvement of the imidazolate ion in the reaction with FePc. In order to obtain evidence about the participation of this species, we studied the reaction of N-methyl and N-n-butylimidazole with FePc, since these derivatives cannot ionise to give an anion. The bis-(N-substituted) products had similar visible spectra[4] to that of FePc(imid)$_2$, and their formation obeyed the same rate law, *i.e.* a second order process (Table I).

TABLE I. Kinetic Results for the Reaction FePc(dmso)$_2$ + Base → FePc(Base)$_2$ in dmso.

Base	k_{25} /l mol^{-1} s^{-1}	$\Delta H^{\star}$/kcal mol^{-1}	$\Delta S^{\star}$/cal k^{-1} mol^{-1}
imid	3.1	17.3 ± 0.5	1.8 ± 1.5
N-Meimid	6.9	18.2 ± 0.5	6.2 ± 1.8
N-n-Butimid	7.9	18.3 ± 0.5	7.1 ± 1.8

Experiments were performed over the temperature range 25 - 45 °C as previously described, and good Eyring plots were obtained. Second order rate constants at 25 °C, and derived activation parameters are similar for all three imidazoles, with the more basic N-substituted derivatives being about twice as reactive as imidazole itself at 25 °C. We therefore conclude that the imidazolate anion is not involved in the reaction between FePc and imidazole in dmso.

Acknowledgement

We thank the S.R.C. for financial support.

References

1 J. G. Jones and M. V. Twigg, *Inorg. Chem., 8,* 2121 (1969).
2 J. G. Jones and M. V. Twigg, *J. Chem. Soc. (A),* 1546 (1970).
3 H. P. Bennetto, J. G. Jones, and M. V. Twigg, *Inorg. Chim. Acta, 4,* 180 (1970).
4 In dmso FePc(imid)$_2$: 662(5.08), 598(4.49), 426(4.30); FePc(NMeimid)$_2$: 660(5.13), 597(4.51), 425 (4.28); FePc(N-n-butimid)$_2$: 660(5.14), 597(4.50), 425(4.29), nm ($\log_{10}\epsilon$).

---

[a] Present address: Chemistry Department, New University of Ulster, Coleraine, Northern Ireland.

[b] Present address: University Chemical Laboratory, Lensfield Road, Cambridge.