Inorganica Chimica Acta, *73* (1983) 95–103

Interaction of Phthalocyaninatoiron(II) with Molecular Oxygen. Kinetics and Mechanism of the Reaction in Dimethyl Sulphoxide

CLAUDIO ERCOLANI*, GENTILINA ROSSI

CNR-ITSE, Area della Ricerca di Roma, via Salaria km 29.500, 00016 Monterotondo Scalo, Rome, Italy

FABRIZIO MONACELLI* and MARIA VERZINO

Istituto di Chimica Generale e Inorganica, Università di Roma, p. le A. Moro 6, 00185 Rome, Italy

Received December 6, 1982

The reaction of phthalocyaninatoiron(II), FePc, with dioxygen in dimethyl sulphoxide solution has been studied kinetically by measuring the visible spectral changes occurring under high concentration conditions (h.c.c.: [FePc] = 1×10^{-4} mol dm^{-3} or higher) and low concentration conditions (l.c.c.: 1×10^{-5} mol dm^{-3} or lower). At h.c.c. the observed spectral variations (a decrease in intensity of the band at 653 nm and a parallel increase of a band at 620 nm) develop with an autocatalytic-like pattern and can be reversed either by nitrogen bubbling or dilution. The insoluble μ-oxo species (FePc)$_2$O is the final reaction product.

Under l.c.c. the spectral changes (a decrease in intensity of the spectrum at all wavelengths within the range 550–750 nm) are associated with an irreversible degradation of the complex. This spectral trend is also observed under h.c.c. when use is made of a free radical inhibitor (2,6-di(tert-butyl)-4-methylphenol).

The whole experimental picture is satisfactorily explained by a mechanism in which an intermediate oxenic species FePcO can either react with FePc, to give reversibly the μ-oxo compound, or can oxidize the solvent (or a species derived from the solvent). In the h.c.c. reaction FePc behaves as an O-atom transfer catalyst.

Introduction

Axial ligation in solution by phthalocyaninatoiron(II), FePc (Pc = phthalocyaninato dianion), with a variety of donor ligands [1–5], including carbon monoxide [6, 7], has been widely investigated, mainly because of the heme-like structure of the molecule.

In extending our interest to the interaction of FePc with molecular oxygen, we reported recently the kinetics of the reaction of this substrate with O$_2$ in 96% sulphuric acid [8]. Moreover, it has been shown that an FePc suspension in a variety of solvents (dimethylformamide, dimethylacetamide, tetrahydrofuran and dioxan) yields a μ-oxo species of formula (FePc)$_2$O upon contact with oxygen or air. This compound (μ-oxo(1)) has been isolated as an air-stable, crystalline solid [9, 10]. Recently [10], a crystalline modification of this compound (*i.e.* μ-oxo (2)) showing different X-ray powder pattern, IR spectrum, and magnetism, has also been isolated and characterised.

(FePc)$_2$O (either μ-oxo(1) or μ-oxo(2) or a mixture of them) is also systematically formed when FePc is suspended in dimethyl sulphoxide (DMSO) in contact with dioxygen or air.

Following our investigation on the kinetics and mechanism of the reaction between FePc and CO in DMSO [7], we describe here the kinetic study of the reaction between FePc and O$_2$ in this solvent.

Experimental

Materials

Commercially available FePc was purified as described elsewhere [8]. Its purity was checked by elemental analyses and magnetic moment (μ_{eff} = 3.87 μ_B) [11]. Argon, nitrogen and oxygen were high purity gases. Oxygen was used as pure gas and as a mixture with either argon or nitrogen; the composition of the mixture was checked by mass spectrometry or determined by measuring under the same pressure the volumes of the gases to be mixed.

DMSO was a C. Erba or Merck product and was purified before use by refluxing over CaH$_2$ and distilling under reduced pressure (b.p. = 65 °C under oil pump vacuum). After distillation the DMSO was washed with argon and stored in a glass bottle under an argon atmosphere.

Solubility of Dioxygen in DMSO

We were not able to find any report on the solubility of dioxygen in DMSO, despite the wide use

---

*Authors to whom correspondence should be addressed.

0020-1693/83/$3.00

of this solvent in various research fields. Thus we measured directly the amount of dioxygen dissolved in a known (25 ml) volume of DMSO, on a conventional volumetric apparatus connected to a vacuum line. The solvent was first subjected to several degassing and N_2-washing cycles before contact with O_2. The volume of dioxygen absorbed at 21.0 °C, under 1 atm of gas pressure, was 1.0 ± 0.1 cm^3 corresponding to a solubility of $(1.7 \pm 0.2) \times 10^{-3}$ mol dm^{-3}. This value is of the expected order of magnitude when compared with the solubility of dioxygen in other organic solvents at the same temperature [12]. In all cases it has been assumed that the solubility of O_2 is proportional to its partial pressure.

Kinetics

The reaction between FePc and O_2 in DMSO was followed kinetically by recording at proper time intervals the spectrum of a solution containing the reactants. The region explored was 550–750 nm where FePc shows absorption maxima at 590 and 653 nm. The reaction solutions were prepared as follows: the iron(II) complex was suspended in DMSO where it dissolves slowly. Contact with dioxygen was avoided, and stirring ensured, by bubbling nitrogen (or argon) through the suspension. From time to time the concentration of FePc dissolved was checked by measuring the absorption at 653 nm ($\epsilon = 7.49 \times 10^4$ mol dm^{-3} cm^{-1}) [13], and when the desired concentration was reached, the suspension was quickly filtered on a Whatman GF/F glass microfibre filter. Controlled dilution of concentrated solutions of FePc showed that Lambert-Beer's law was strictly obeyed in the range 3×10^{-4}–1×10^{-5} mol dm^{-3}.

Pure dioxygen (or inert gas-dioxygen mixture) was bubbled through the solution at room temperature for 5–8 min, this time being sufficient to ensure saturation. The solution was then poured into a 10-mm or 1-mm spectrophotometric cell (according to the iron(II) concentration) and the cell was tightly stoppered. Care was taken to wash the inside of the cell with dioxygen (or its mixture) and to fill the cell almost completely with the solution to minimize any effect due to re-equilibration of the solution with the gas phase. The cell was then placed in the cell compartment of a Perkin Elmer 555 recording spectrophotometer, thermostatted at 21.0 ± 0.1 °C.

Results

The most remarkable aspect of the reaction between FePc and O_2 in DMSO is that the reaction picture changes drastically, both from the kinetic and the stoichiometric point of view, when the concentration of the iron(II) complex is changed merely by a factor of ten, *i.e.* from *ca.* 1×10^{-4} to *ca.* 1×10^{-5} mol dm^{-3}. For this reason it is worth examining separately the results under low concentration conditions (l.c.c.: 1×10^{-5} mol dm^{-3} or less) and under high concentration conditions (h.c.c.: 1×10^{-4} mol dm^{-3} or more).

Reaction under l.c.c.

When the reaction between FePc and O_2 in DMSO is carried out at an initial FePc concentration of *ca.* 1×10^{-5} mol dm^{-3} (or less) the spectrum of FePc, characterised by the intense band at 653 nm, steadily decreases at all wavelengths and the final spectrum is virtually flat (Fig. 1). The reaction is very slow, the fastest runs ($P_{O_2} = 1$ atm) having half-lives of more than 50 h at 21 °C. Good first-order plots were obtained in all cases and the pseudo first-order rate constants are reported against the (constant) dioxygen concentration in Fig. 2. It appears clearly that the reaction is also first-order in dioxygen, with a second-order rate constant $k' = (2.2 \pm 0.1) \times 10^{-3}$ s^{-1} mol^{-1} dm^3.

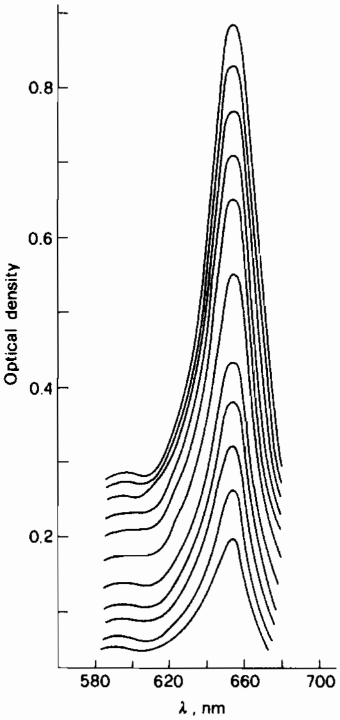

Fig. 1. Spectral evolution of an FePc solution under l.c.c. in the presence of dioxygen. $[FePc]_0 = 1.2 \times 10^{-5}$ mol dm^{-3}; $[O_2] = 1.7 \times 10^{-3}$ mol dm^{-3}; temperature: 21.0 °C.

Reaction Product(s) and Reversibility

The concentration level of FePc under l.c.c. was too low for a separation and characterisation of the reaction product(s) to be allowed. A careful examination of the solution under magnification showed the

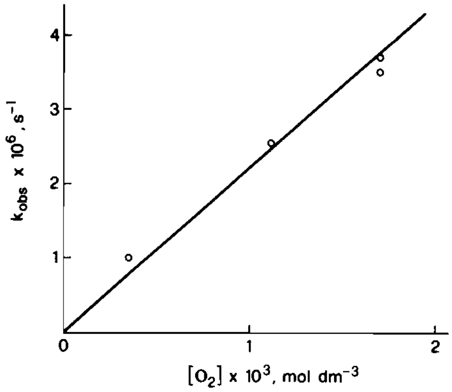

Fig. 2. Reaction under l.c.c.. Linear dependence of the observed pseudo first-order rate constant on dioxygen concentration.

presence of extremely small amounts of a white, fluffy, precipitate. This latter, upon dissolution in pyridine, did not show any evidence for the presence of Py_2FePc[≠]. Furthermore, the reaction is irreversible since bubbling nitrogen through the solution at any stage never caused the spectrum to shift again to that of FePc.

Although we have no indication of the nature of the reaction product(s), it seems most likely that the l.c.c. process is an irreversible, disruptive oxidation of the phthalocyaninato ring.

Reaction under h.c.c.

When a DMSO solution of FePc in the concentration range 1×10^{-4}–4×10^{-4} mol dm^{-3} (*i.e.*, only ten times the concentration limit of the experiments described above) is saturated at 21.0 °C with dioxygen (or a mixture of O_2 with an inert gas) under normal pressure, the spectrum changes with time as shown in Fig. 3 (spectra a–f). These spectra define three isosbestic points, one of which (630 nm) is very sharp. As long as all the isosbestic points are maintained, the increasing absorbance at 620 nm is a linear function of the decreasing absorption at 653 nm. After a while (generally, at *ca.* 60–70% of reaction, as estimated from the final spectrum, see below) the isosbestic point at 630 nm is lost (spectrum g) and the spectrum starts decreasing at all wavelengths (spectra h and i). Inspection of the solution under magnification at late stages of reaction shows the presence of purple crystals which exhibit a positive pyridine test[≠].

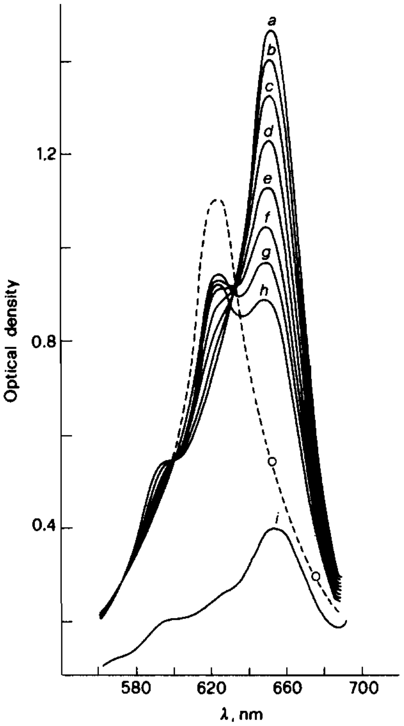

Fig. 3. Spectral evolution of an FePc solution in the presence of dioxygen, under h.c.c.. $[FePc]_0 = 2 \times 10^{-4}$ mol dm^{-3}; $[O_2] = 1.7 \times 10^{-3}$ mol dm^{-3}; temperature: 21.0 °C. Spectra a–h are taken every 5 min; spectrum i, taken after 120 min, shows the effect of the precipitation of the oxygenated product. The dashed line is the infinite time spectrum constructed as described in the text.

Experiments carried out with adequately large solution samples allowed the solid material to be recovered and identified as the μ-oxo oligomer $(FePc)_2O$ [9, 10]. This species is totally insoluble in DMSO so that it should precipitate in the earliest stages of the autoxidation process. However, it should be noted that the experiments are carried out near the freezing point of the solvent (18.4 °C) where viscosity may efficiently retard the formation of crystals. Consistently, at higher temperatures (*e.g.*, 30 °C) precipitation starts at lower reaction percents.

'Reversibility'

The original spectrum of FePc can be reobtained from an oxygenated solution by merely bubbling an inert gas. Typically, more than 90% of the original FePc is re-obtained in this way, provided that extensive precipitation had not occurred before. Also, care had to be taken to use an initial concentration of FePc not higher than 1.5×10^{-4} mol dm^{-3} since above this limit both the oxygenation and the precipitation become too fast to allow any further handling of the solution. Even in the most favourable cases some precipitation of the μ-oxo derivative could not

---

[≠] FePc adducts with a variety of ligands, when dissolved in excess pyridine, yield invariably the species Py_2FePc, which may be easily detected on the basis of its spectrum (λ_{max} = 655 nm) [13]. On our experience, a positive reaction with pyridine demonstrates that the FePc moiety is present in the compound tested. On the other hand, a negative pyridine test strongly suggests that the phthalocyaninatoiron(II) has undergone an irreversible chemical modification.

be avoided, with a reduction in the capability of the solution to undergo successive oxygenation-deoxygenation cycles.

The initial spectrum of FePc can also be reobtained by diluting the oxygenated mixture. Solutions of the iron(II) complex ([FePc] = 1×10^{-4} mol dm^{-3}) were allowed to react with dioxygen as described above. Immediately after the isosbestic point at 630 nm was lost, an aliquot (50–250 μl) of the solution was withdrawn by means of a microsyringe and quickly diluted to 3.00 ml in a 1-cm spectrophotometric cell with oxygen-containing DMSO, so as to obtain an iron(II) concentration lower than 1×10^{-5} mol dm^{-3} whilst the O_2 concentration remained constant. The spectrum of the resulting solution was recorded and found to change slowly to that of free FePc, following a pattern almost exactly inverse of that shown in Fig. 3. No instantaneous changes were observed soon after dilution, once allowance was made for the decrease in concentration. The kinetics were first-order and independent of dioxygen concentration, with an average rate constant of $(2.2 \pm 0.2) \times 10^{-4}$ s^{-1}. The amount of FePc released by dilution was 90–95% of the original amount.

Eventually, on a much larger time scale, the FePc solution showed the spectral evolution characteristic of the low concentration runs.

The Infinite Time Spectrum

Because of precipitation, the infinite time spectrum of the solution could never be measured directly. Hence, the following procedure was used to obtain a reasonable estimate of the final spectrum. As the reaction proceeds, the maximum at 653 nm eventually becomes a shoulder at *ca.* 650 nm on the band centred at 620 nm. Occasionally, and for runs carried out at the highest FePc concentrations, this shoulder was very smooth and the 620 nm band approached a symmetric shape. This fact was taken as an indication that the shoulder was indeed due to a small (and variable) amount of starting FePc. On this assumption, and taking advantage of the presence of three isosbestic points, an 'infinite time' symmetric spectrum was constructed for each run (dashed line of Fig. 3). It is worth noting that this spectrum is similar to that obtained immediately after dissolving the μ-oxo compound $(FePc)_2O$ in pyridine and before it slowly changes to the spectrum of Py_2FePc [14].

Inhibition Experiments

Some h.c.c. runs were carried out after addition of variable amounts of 2,6-di(tert-butyl)-4-methylphenol [15] (DBMP) to the reacting solution. The h.c.c. spectral evolution of Fig. 3 was totally suppressed at DBMP concentration levels of *ca.* 1×10^{-4} mol dm^{-3}, and the mixture behaved according to a l.c.c.-like pattern.

The pseudo-first order rate constants so obtained were practically insensitive to the amount of inhibitor up to *ca.* 1×10^{-3} mol dm^{-3}.

Kinetic Law

When the absorbance at 653 nm (where the change is largest) is plotted as a function of time, under any dioxygen partial pressure, an S-shaped curve with non-zero initial slope is obtained (Fig. 4). Since the presence of several isosbestic points makes the accumulation of intermediates species very unlikely, this S-shaped profile suggests some sort of autocatalytic process [16].

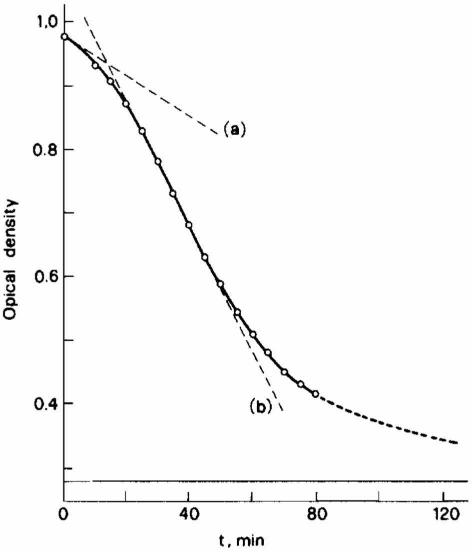

Fig. 4. Absorbance at 650 nm as a function of time. $[FePc]_0 = 1.3 \times 10^{-4}$ mol dm^{-3}; $[O_2] = 1.7 \times 10^{-3}$ mol dm^{-3}. The horizontal line is the asymptotic limit calculated on the basis of the final spectrum obtained as described in the text. The experimental points are reported as long as the 630 nm isosbestic point is present. The dashed straight lines correspond to the initial rate (a) and the rate at 50% of reaction (b).

Hence, at constant dioxygen concentration, it may be reasonably postulated that:

$$-\frac{d[FePc]}{dt} = k''[FePc]^m + k'''[FePc]^n[(FePc)_2O]^p \tag{1}$$

where the second term accounts for the autocatalytic effect. Since, in the absence of intermediates, the mass balance has the simple form $[FePc]_0 = [FePc] + 2[(FePc)_2O]$, at any fixed percent of reaction eqn. 1 reduces to:

$$-\frac{d[FePc]}{dt} = A[FePc]_0^m + B[FePc]_0^{(n+p)}. \tag{2}$$

with A and B which are functions of the reaction percent and of k″ and k‴, respectively. Two conditions may be chosen which may be easily handled: the $t = 0$ rate, where eqn. 1 reduces to the form:

$$-\left(\frac{d[FePc]}{dt}\right)_0 = k''[FePc]_0^m \qquad (3)$$

and the rate at 50% of reaction, where:

$$-\left(\frac{d[FePc]}{dt}\right)_{50} = \frac{k''}{2^m}[FePc]_0^m + \frac{k'''}{2^{n+2p}}[FePc]_0^{(n+p)}. \qquad (4)$$

For each run the left-hand-side of eqns. 3 and 4 have been estimated graphically from the slopes at zero time and at 50% of reaction, respectively, on the *D vs.* time plot (as shown in Fig. 4) using the equation:

$$\frac{d[FePc]}{dt} = \frac{dD}{dt} \times \frac{[FePc]_0}{D_0 - D_\infty}$$

TABLE I. Substrate Initial Concentration and Instantaneous Rates (zero time and 50% of reaction rates) for the Runs under h.c.c. and Unitary Dioxygen Pressure. Temperature: 21.0 °C.

$[FePc]_0 \times 10^4$ (mol dm^{-3})	$-\frac{(dD/dt)_0}{D_0 - D_\infty} \times 10^4$ (s^{-1})	$-\frac{(dD/dt)}{D_0 - D_\infty} \times 10^4$ (s^{-1})
1.02	0.42	0.98
1.12	0.35	0.98
1.12	0.45	1.00
1.16	0.58	0.87
1.19	0.48	0.95
1.24	0.73	1.21
1.37	0.37	0.96
1.61	0.57	1.38
2.11	1.16	2.33
2.12	0.93	2.00
2.13	0.88	2.08
2.34	1.16	2.50
2.80	1.14	2.66
2.88	1.66	3.00
3.75	1.71	3.94

TABLE II. Substrate Initial Concentration and 50% -of-Reaction Rates for Runs under h.c.c. and Different Dioxygen Pressures. Temperature: 21.0 °C.

$[FePc]_0 \times 10^4$ (mol dm^{-3})	$[O_2] \times 10^3$ (mol dm^{-3})	$-\frac{d[FePc]/dt}{[FePc]_0^2}$ (s^{-1} mol^{-1} dm^3)
	1.7	1.0[a]
1.09	1.44	0.78
1.22	1.11	0.70
1.24	1.11	0.67
1.27	0.81	0.39
2.92	0.81	0.43

[a] Slope of the plot of Fig. 6.

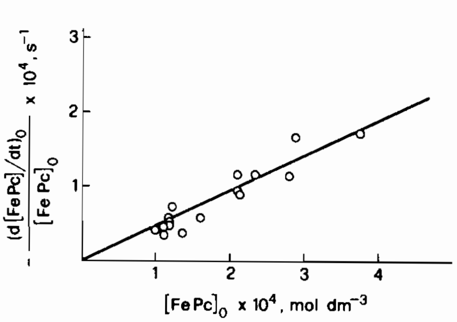

Fig. 5. $-(d[FePc]/dt)_0/[FePc]_0$ ratio as a function of $[FePc]_0$ for h.c.c. runs. The data are taken from Table I.

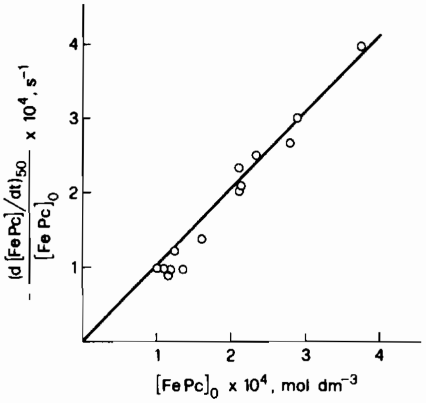

Fig. 6. $-(d[FePc]/dt)_{50}/[FePc]_0$ ratio as a function of $[FePc]_0$ for h.c.c. runs. Data from Table I.

The rates measured at 50% of reaction are generally more accurate (± 10%) than the initial rates which suffer an intrinsically larger inaccuracy (± 20%)†. The relevant data so obtained are reported in Tables I and II. Figures 5 and 6 show the plots of $-(d[FePc]/dt)_0/[FePc]_0$ and $-(d[FePc]/dt)_{50}/[FePc]_0$, respectively, *vs.* $[FePc]_0$, for runs at $[O_2] = 1.7 \times 10^{-3}$ mol dm^{-3}. Within the experimental error they are both straight lines of zero intercept and slopes 0.43 ± 0.07 and 1.05 ± 0.06 s^{-1} mol^{-1}, respectively.

To be consistent with the plots of Figs. 5 and 6, eqn. 1 should have the following form:

$$-\frac{d[FePc]}{dt} = k''[FePc]^2 + k'''[FePc][(FePc)_2O] \qquad (5)$$

---

† It should be remembered (see Experimental) that in all cases the oxygenation process was followed after *ca.* 5 min of O_2 bubbling during which the dioxygen concentration was not constant. Consequently, for the first few minutes the actual shape of the plot of Fig. 4 is somewhat imprecise.

Thus, $k'' = 0.43\ s^{-1}\ mol^{-1}\ dm^3$, $k''/4 + k'''/8 = 1.05\ s^{-1}\ mol^{-1}\ dm^3$ and, hence, $k''' = 7.5\ s^{-1}\ mol^{-1}\ dm^3$.

Figure 7 reports the ratio $-(d[FePc]/dt)_{50}/[FePc]_0^2 = k''/4 + k'''/8$ as a function of $[O_2]$. Again, a straight line of zero intercept is obtained, indicating that both k'' and k''' are linear function of $[O_2]$.

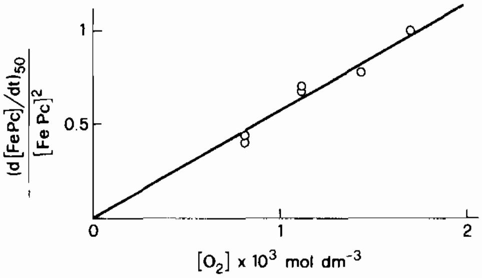

Fig. 7. $-(d[FePc]/dt)_{50}/[FePc]_0^2$ ratio as a function of dioxygen concentration for h.c.c. runs. Data from Table II.

Discussion

The reaction picture arising from this study has complex contours. Nevertheless, the experimental behaviour of the $FePc + O_2 + DMSO$ system described in this paper was reproducible and independent of the 'history' of the materials employed. Only precipitation phenomena, particularly those occurring at h.c.c., were relatively unpredictable, as often happens when dealing with metastable systems.

Despite the complexity of the pattern observed, we believe that the main aspects of this reaction are now sufficiently clear and may be rationalised.

The l.c.c. data are in agreement with the reaction sequence:

$$FePc + O_2 \xrightarrow{\text{step 1}} FePcO_2 \xrightarrow{\text{step 2}} X \qquad (6)$$

(X stands for the unknown oxidation product(s)), where either step 1 may be rate determining and step 2 is fast or step 1 is a fast, left-shifted equilibrium, and step 2 is slow. In both cases the observed rate of reaction would be, in fact:

$$-\frac{d[FePc]}{dt} = k'[FePc][O_2] \qquad (7)$$

in agreement with the experiments.

The change in kinetic and stoichiometric behaviour shown by the system under h.c.c. can hardly be explained by considering an alternative to step 1, which then is common to both l.c. and h.c. situations.

Thus, a third step must be postulated leading from the intermediate adduct $FePcO_2$ to the final μ-oxo species:

$$FePc + O_2 \xrightarrow{\text{step 1}} FePcO_2 \begin{cases} \xrightarrow{\text{step 2}} X \\ \xrightarrow[\text{step 3}]{} (FePc)_2O \end{cases} \qquad (8)$$

The h.c.c. experiments are only consistent with step 1 being a fast equilibrium (largely left-hand shifted) and steps 2 and 3 rate determining. In fact, were step 1 slow and (consequently) steps 2 and 3 fast, the reaction would obey the same overall second-order kinetic law under any FePc concentration.

Inert-gas bubbling experiments may suggest that steps 1 and 3 are reversible; since four FePc molecules per mole of O_2 are involved along the overall step 1 + step 3 pathway:

$$4FePc + O_2 \rightleftharpoons 2FePcOFePc \qquad (9)$$

a shift of the equilibrium to the right, on increasing the initial FePc concentration, can be predicted. However, the stoichiometry of eqn. 9 is by far insufficient to account for the remarkable concentration effect observed. The unrealistic existence of reactive aggregates $(FePc)_n$ with $n > 10$ or the equally unrealistic formation of $((FePc)_2O)_n$ polymers, again with n being a large number, would be necessary to explain the results on a mass-law basis. No evidence whatsoever has been obtained of such aggregates and even a previous report on the formation of $(FePc)_2$ dimers [17] under experimental conditions very close to present conditions appears to be erroneous§.

Hence, the observed effect must be essentially kinetic in nature and, thus, intimately related to the mechanism. This latter should also account for the inhibition effect by DBMP.

We will show that the following reaction sequence accounts satisfactorily for all the observations (axial DMSO molecules are omitted for simplicity):

$$FePc + O_2 \overset{K_1}{\rightleftharpoons} FePcO_2 \qquad (10)$$

$$FePcO_2 \xrightarrow{k,\ \text{slow}} \text{oxid. prod. (s) } X\ (k' = kK_1) \qquad (11)$$

$$FePcO_2 + FePc \overset{K_2}{\rightleftharpoons} (FePc)_2O_2 \qquad (12)$$

$$(FePc)_2O_2 \underset{k_{-1}}{\overset{k_1,\ \text{slow}}{\rightleftharpoons}} 2FePcO \qquad (13)$$

$$FePcO + FePc \underset{k_{-2},\ \text{slow}}{\overset{k_2,\ \text{fast}}{\rightleftharpoons}} (FePc)_2O \qquad (14)$$

$$\underset{\text{(catalyst)}}{FePcO_2 + (FePc)_2O} \underset{-FePc;\ k'_{-1}}{\overset{+FePc;\ k'_1,\ \text{slow}}{\rightleftharpoons}} 2FePcO + \underset{\text{(catalyst)}}{(FePc)_2O} \qquad (15)$$

$$FePcO + R \xrightarrow{k_R,\ \text{fast}} FePc + RO \qquad (16)$$

---

§The spectral changes observed in the range 10^{-5}–10^{-4} mol dm^{-3} and assigned to the monomer-dimer equilibrium were clearly due to the unrecognized oxygenation of FePc.

The species $FePcO_2$ and $(FePc)_2O_2$ postulated in the above set of reactions are analogous to now well-established intermediates in autoxidation processes of strictly related Fe(II) complexes such as Fe(II)-porphyrins [18]. Evidence for ferryl compounds of the type FePO (P = porphyrinato dianion) has also been reported [19]. Equation 15 has been included to account for the autocatalytic effect and eqn. 16 describes the reaction of a reducing species R capable of abstracting the oxygen from the intermediate FePcO (supposed to be very reactive) and restoring the starting FePc. The result of eqn. 15 is then to lower the net rate of formation of $(FePc)_2O$ by competing with eqn. 14 (forward). R may be the solvent itself, or any species in fast equilibrium with it, the concentration of which may be considered constant.

Let us ignore, at this stage, the slow reaction 11; on the basis of the reactions 10, 12–16 it can be demonstrated (see the Appendix) that, under steady state conditions for the oxenic intermediate FePcO, the rate of reaction is:

$$-\frac{d[FePc]}{dt} = \frac{4k_f[FePc]^2 + 4k'_f[FePc][(FePc)_2O] -}{1 + k_R[R]/k_2[FePc]}$$

$$\frac{- 2(k_R[R]/k_2[FePc])k_{-2}[(FePc)_2O]}{1 + k_R[R]/k_2[FePc]} \qquad (17)$$

where $k_f = k_1K_1K_2[O_2]$ and $k'_f = k'_1K_1[O_2]$.

It is immediately evident that eqn. 17 is equivalent to eqn. 5 for low values of the ratio $k_R[R]/k_2[FePc]$, *i.e.* for 'high' values of [FePc]. Let us assume that this is the case when $[FePc] \geqslant 1 \times 10^{-4}$ mol dm^{-3}. Comparison between eqn. 5 and eqn. 17 yields:

$$k_f = k''/4 = 0.11\ s^{-1}\ mol^{-1}\ dm^3$$

and

$$k'_f = k'''/4 = 1.9\ s^{-1}\ mol^{-1}\ dm^3$$

Moreover, within the framework of the mechanism proposed, the first-order process which takes place after dilution of partially oxygenated h.c.c. solutions can only be identified with the reverse of eqn. 14: hence, $k_{-2} = 2.2 \times 10^{-4}\ s^{-1}$ (see Results). Using eqn. 17 and treating $k_R[R]/k_2$ as an adjustable parameter, it can be shown that if this ratio is of the order of 5×10^{-6} mol dm^{-3}, solutions having $[FePc]_0 \geqslant 1 \times 10^{-4}$ mol dm^{-3} do react at a relatively high rate to give $(FePc)_2O$ virtually as the only spectrophotometrically detectable product (see Fig. 8a). On the other hand, when $[FePc]_0$ is lowered to 1×10^{-5} mol dm^{-3} the rate of formation of $(FePc)_2O$ drops drastically to become zero after the formation of a few percent of the μ-oxo species. Reaction 11 becomes then the dominant (virtually unique) process (see Fig. 8b).

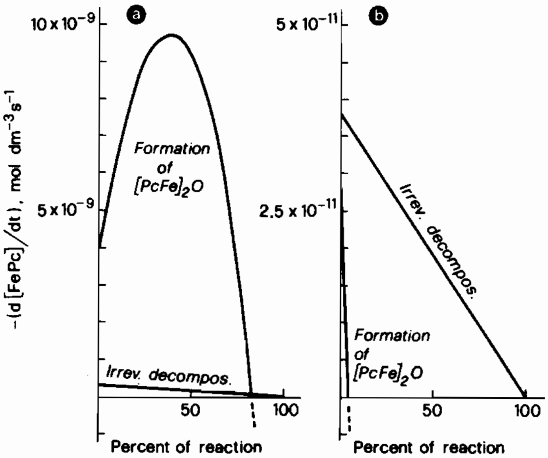

Fig. 8. Rate of formation of FePcOFePc (a) for $[FePc]_0 = 1 \times 10^{-4}$ mol dm^{-3} (h.c.c.) and for (b) $[FePc]_0 = 1 \times 10^{-5}$ mol dm^{-3} (l.c.c.), as calculated according to eqn. 17. The parallel rate of decomposition of FePc is also shown in both cases.

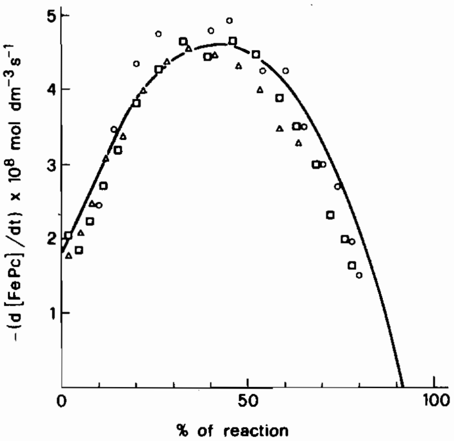

Fig. 9. Instantaneous rates for μ-oxo compound formation under h.c.c.. The points refer to three independent experiments at constant $[FePc]_0$. The line is calculated according to eqn. 17.

Equation 17 has been tested by comparing calculated with experimental instantaneous h.c.c. rates as reported in Fig. 9. The degree of fit is excellent and might even be improved by means of a best fitting procedure.

In view of the complexity of the reactivity picture described, such an excellent fit of calculated to experimental results lends strong support to the mechanism proposed. The latter also explains the results of the dilution experiments. When an FePc solution is oxygenated under h.c.c. up to 60–70% of reaction the rate $-(d[FePc]/dt)$ is still positive (Fig. 8a). After diluting by a factor of ten the rate becomes negative (*i.e.*, the μ-oxo compound decomposes back to FePc).

The spectrum of FePc can also be restored by bubbling an inert gas through the solution. Although this is obviously the consequence of the elimination of dioxygen from the solution, it does not necessarily imply reversibility towards O_2, since the same effect will be observed even if reactions 13 and 15 are irreversible (*i.e.*, $k_{-1} = k'_{-1} = 0$). In fact, since both k_f and k'_f are proportional to $[O_2]$, when the latter goes to zero the rate $-d[FePc]/dt$ would again become negative and FePc would be produced irreversibly through the sequence:

$$(FePc)_2O \longrightarrow FePcO + FePc \xrightarrow{R} 2FePc + RO$$

The inhibitory effect of DBMP on the h.c.c. pattern is not completely understood. Within the framework of the mechanism proposed (eqns. 10–16) there are at least two species which could be considered as potential radicals, *i.e.* $FePcO_2$ (with an Fe(III)–superoxo-like structure) and FePcO (with an Fe(III)–O(–1) structure). Some ESR measurements on frozen samples of oxygenated FePc solutions did show a resonance signal at 3240 gauss but its very low intensity, close to the sensitivity limits of the instrument, prevented any further study. Since the addition of DBMP does not seem to disturb appreciably the rate of oxidation of FePc via eqns. 10 and 11, we feel that $FePcO_2$ is not involved in the inhibition mechanism. Additional work is clearly needed on this point.

Finally, it is most interesting to recognize that the set of reactions 10, 12–16 represents a cyclic process where dioxygen is tranferred as single atoms to a reducing substrate, under ambient conditions, the FePc acting as a homogeneous catalyst. This mechanism is very similar to that proposed by Chin *et al.* [19] for the Fe(TTP)-catalysed formation of Ph_3PO from O_2 and Ph_3P in toluene (TTP = meso-tetraphenylporphyrinato anion). The ferryl species Fe(TTP)O was indicated as the reactive atomic-oxygen carrier. The most relevant difference between the two reactions seems to be that whilst $[Fe(TTP)]_2O$ represents the final, irreversible, fate for Fe(TTP)O, the analogous phthalocyaninato μ-oxo species is reversible and may generate back the oxidizing ferryl intermediate FePcO. Indeed, preliminary experiments show that Ph_3P is oxidized to Ph_3PO by reaction with $(FePc)_2O$ in pyridine-containing toluene [20].

Work is in progress to study the catalytic properties of FePc in the light of the mechanism discussed here.

Acknowledgement

This work has been financed in part by the CNR Project "Chimica Fine e Secondaria".

References

1 J. G. Jones and M. V. Twigg, *Inorg. Chem., 8,* 2120 (1969).

2 H. P. Bennetto, J. G. Jones and M. V. Twigg, *Inorg. Chim. Acta, 4,* 180 (1970).

3 J. G. Jones and M. V. Twigg, *Inorg. Chim. Acta, 10,* 103 (1974).

4 J. G. Jones and M. V. Twigg, *J. Chem. Soc., Dalton Trans.,* 1709 (1978).

5 J. Martinsen, M. Miller, D. Troian and D. A. Sweigart, *Inorg. Chem., 19,* 2162 (1980).

6 D. V. Stines and B. R. James, *J. Am. Chem. Soc., 96,* 2733 (1974).

7 C. Ercolani, F. Monacelli, G. Pennesi, G. Rossi, E. Antonini, P. Ascenzi and M. Brunori, *J. Chem. Soc., Dalton Trans.,* 1120 (1981).

8 C. Ercolani, G. Rossi and F. Monacelli, *Inorg. Chem., 18,* 712 (1979).

9 C. Ercolani, G. Rossi and F. Monacelli, *Inorg. Chim. Acta, 44,* L215 (1980).

10 C. Ercolani, M. Gardini, F. Monacelli, G. Pennesi and G. Rossi, *Inorg. Chem.*, accepted for publication.

11 H. Senff and W. Klemm, *J. Prakt. Chem., 154,* 73 (1939).

12 W. F. Linke, 'Solubilities. Inorganic and metal-organic compounds', II, Am. Chem. Soc., Washington D.C., 1965, pp. 1228–1239.

13 B. W. Dale, *Trans. Farad. Soc., 65,* 331 (1969).

14 C. Ercolani, F. Monacelli and G. Rossi, unpublished results.

15 A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.,* 3211 (1953).

16 A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism', 2nd ed., J. Wiley, New York, 1961, p. 19.

17 J. G. Jones and M. V. Twigg, *Inorg. Nucl. Chem. Lett., 44,* 305 (1972).

18 See B. R. James, 'The Porphyrins', V, Physical Chemistry, Part C, D. Dolphin Ed., Chapt. 6, p. 205, and references therein.

19 D. H. Chin, G. N. La Mar and A. L. Balch, *J. Am. Chem. Soc., 102,* 5945 (1980), and references therein.

20 C. Ercolani, M. Gardini, G. Pennesi and G. Rossi, unpublished results.

Appendix

The steady-state condition applied to the FePcO species yields:

$$\frac{d[FePcO]}{dt} = 0 = -2(k_{-1} + k'_{-1}[(FePc)_2O])[FePcO]^2 - (k_2[FePc] + k_R[R])[FePcO] + 2k_f[FePc]^2 +$$

$$+ [(FePc)_2O](k_{-2} + 2k'_f[FePc])$$

where both equilibria 10 and 12 are assumed to be largely left-hand shifted and $k_f = k_1K_1K_2[O_2]$ and $k'_1 = k'_1K_1[O_2]$. By solving the quadratic equation we obtain:

$$[\mathrm{FePcO}] = -\frac{k_2[\mathrm{FePc}] + k_R[R] - \{(k_2[\mathrm{FePc}] + k_R[R])^2 + 8(k_{-1} + k'_{-1}[(\mathrm{FePc})_2O])(2k_f[\mathrm{FePc}]^2}{4(k_{-1} + k'_{-1}[(\mathrm{FePc})_2O])} +$$

$$+\frac{k_{-2}[(\mathrm{FePc})_2O] + 2k'_f[\mathrm{FePc}][(\mathrm{FePc})_2O])\}^{1/2}}{4(k_{-1} + k'_{-1}[(\mathrm{FePc})_2O])}$$

which may be conveniently rewritten in the form:

$$\{\mathrm{FePcO}] = -\frac{k_2[\mathrm{FePc}] + k_R[R]}{4(k_{-1} + k'_{-1}[(\mathrm{FePc})_2O])} \times$$

$$\times\left[1 - \left\{1 + \frac{8(k_{-1} + k'_{-1}[(\mathrm{FePc})_2O])(2k_f[\mathrm{FePc}]^2 + k_{-2}[(\mathrm{FePc})_2O] + 2k_f[\mathrm{FePc}][(\mathrm{FePc})_2O])}{(k_2[\mathrm{FePc}] + k_R[R])^2}\right\}^{1/2}\right] \tag{1A}$$

The concentration of FePcO must be very small and the square root close to unity. Since $(1 + \epsilon)^{1/2} \approx 1 + \epsilon/2$ for $\epsilon \ll 1$, eqn. 1A may be approximated to:

$$[\mathrm{FePcO}] = \frac{2k_f[\mathrm{FePc}]^2 + k_{-2}[(\mathrm{FePc})_2O] + 2k'_1[\mathrm{FePc}][(\mathrm{FePc})_2O]}{k_2[\mathrm{FePc}] + k_R[R]} \tag{2A}$$

The rate of formation of $(\mathrm{FePc})_2O$

$$\frac{d[(\mathrm{FePc})_2O]}{dt} = k_2[\mathrm{FePcO}][\mathrm{FePc}] - k_{-2}[(\mathrm{FePc})_2O] \tag{3A}$$

Combining eqn. 2A and eqn. 3A and considering that $d[(\mathrm{FePc})_2O]/dt = -(1/2)(d[\mathrm{FePc}]/dt)$, after straightforward manipulations we obtain:

$$-\frac{d[\mathrm{FePc}]}{dt} = \frac{4k_f[\mathrm{FePc}]^2 + 4k'_f[\mathrm{FePc}][(\mathrm{FePc})_2O] - 2(k_R[R]/k_2[\mathrm{FePc}])k_{-2}[(\mathrm{FePc})_2O]}{1 + k_R[R]/k_2[\mathrm{FePc}]}$$