and -(IV), but rather two vicinal hydroxyls in a manner analogous to sorbitol.

The enhancement of the catalytic effect of manganese for oxygen pulping in alkaline solution by the addition of sorbitol may be due to the increased solubilization of the Mn(III) and Mn(IV) oxidation states. This, in turn, would allow the manganese ions to function as more efficient oxygenation catalysts and electron transfer agents for selective delignification.

The manganese–polyhydroxy complexes appear to provide an efficient method for the generation of peroxide anion in alkaline solution from molecular oxygen. However, the ability of these complexes to act as efficient oxygenation catalysts remains to be established.

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Registry No. Sorbitol, 50-70-4; D-gluconic acid, 526-95-4; D-glucaric acid, 87-73-0; L-tartaric acid, 87-69-4; (+)-sucrose, 57-50-1; Mn, 7439-96-5.

References and Notes

(1) R. L. Heath, *Int. Rev. Cytol.*, **34**, 49 (1973).
(2) G. M. Cheniae, *Annu. Rev. Plant Physiol.*, **21**, 467 (1970).
(3) R. Radmer and G. M. Cheniae in "Primary Processes", in press.
(4) R. E. Blankenship, Ph.D. Dissertation, University of California, Berkeley, CA, 1974.
(5) B. B. Keele, J. M. McCord, and I. Fridovich, *J. Biol. Chem.*, **245**, 6176 (1970).
(6) M. Pick, J. Rabani, F. Yost, and I. Fridovich, *J. Am. Chem. Soc.*, **96**, 7329 (1974).
(7) R. Radmer and G. M. Cheniae, *Biochem. Biophys. Acta*, **253**, 182 (1971).
(8) T. Wydrzynski, N. Zumbulyadis, P. G. Schmidt, and G. Govindjee, *Biochem. Biophys. Acta*, **408**, 349 (1975).
(9) T. Wydrzynski, N. Zumbulyadis, P. G. Schmidt, H. S. Gutowski, and G. Govindjee, *Proc. Natl. Acad. Sci. USA*, **73**, 1196 (1976).
(10) J. Doležal and F. J. Langmyhr, *Anal. Chim. Acta*, **61**, 73 (1972).
(11) N. Chughtai, J. Doležal, and J. Zýka, *Microchem. J.*, 20 (1975).
(12) G. Donoso, J. Doležal, and J. Zýka, *J. Electroanal. Chem. Interfacial Electrochem.*, **49**, 461 (1974).
(13) J. Doležal, E. Juláková, M. Černý, and M. Kopanica, *J. Electroanal. Chem. Interfacial Electrochem.*, **52**, 261 (1974).
(14) J. Doležal and H. Kekulova, *J. Electroanal. Chem. Interfacial Electrochem.*, **69**, 239 (1976).
(15) B. L. Velikov and J. Doležal, *J. Electroanal. Chem. Interfacial Electrochem.*, **71**, 91 (1976).
(16) J. L. Minor, unpublished results, Forest Products Laboratory, U.S. Department of Agriculture, Madison, WI, 1978.
(17) L. L. Landucci and N. Sanyer, *Tappi*, **57**, 97 (1974).
(18) M. E. Bodini, L. A. Willis, T. L. Riechel, and D. T. Sawyer, *Inorg. Chem.*, **15**, 1538 (1976).
(19) K. D. Magers, C. G. Smith, and D. T. Sawyer, *Inorg. Chem.*, **17**, 515 (1978).
(20) M. E. Bodini and D. T. Sawyer, *J. Am. Chem. Soc.*, **98**, 8366 (1976).
(21) D. T. Sawyer, M. E. Bodini, L. A. Willis, T. L. Riechel, and K. D. Magers, *Adv. Chem. Ser.*, **No. 162**, 330–49 (1977).
(22) A. Goolsby and D. T. Sawyer, *Anal. Chem.*, **39**, 411 (1967).
(23) D. T. Sawyer and J. L. Roberts, Jr., "Experimental Electrochemistry for Chemists", Wiley-Interscience, New York, 1974.
(24) M. F. Rettig, private communication, University of California, Riverside, CA, 1975.
(25) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(26) B. N. Figgis and J. Lewis in "Progress in Inorganic Chemistry", Vol. 6, F. A. Cotton, Ed., Interscience, New York, 1964, pp 37–240.
(27) G. Brauer, "Handbook of Preparative Inorganic Chemistry", Vol. 2, 2nd ed., Academic Press, New York, 1965, p 1469.
(28) T. S. Davis, J. P. Fackler, Jr., and M. J. Weeks, *Inorg. Chem.*, **7**, 1994 (1968).
(29) J. Summers, Ph.D. Dissertation, University of Florida, 1968.
(30) R. Dingle, *Acta Chem. Scand.*, **20**, 33–44 (1966).
(31) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes", Addison-Wesley, Reading, MA, 1962.
(32) C. K. Jørgensen, *Acta Chem. Scand.*, **12**, 1539 (1958).
(33) E. I. Ochiai, *J. Inorg. Nucl. Chem.*, **35**, 3375 (1973).
(34) J. Klepetář and K. Štulik, *J. Electroanal. Chem.*, **55**, 255 (1974).
(35) P. Crabbé, "ORD and CD in Chemistry and Biochemistry. An Introduction", Academic Press, New York, 1972.

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Interaction of Iron(II) Phthalocyanine with Molecular Oxygen in Concentrated Sulfuric Acid: Kinetics and Mechanism

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The reaction of iron(II) phthalocyanine, FePc, with O_2 in concentrated (96%) sulfuric acid has been studied kinetically. The overall reaction is a two-step process. The first step is reversible and follows a kinetic law of the type rate = $a[O_2][FePc]/(1 + b[O_2])$, while the second step is irreversible and takes place with a rate constant $k_{II} = k_{II}' + k_{II}''[O_2]$. The experimental data can be satisfactorily explained by assuming that FePc, presumably tetraprotonated and with HSO_4^- ions coordinated at the axial positions of Fe(II), generates a pentacoordinate intermediate (by loss of HSO_4^-) which then reacts with dioxygen. The 1:1 O_2·FePc adduct then gives a 1:2 species through a fast reaction with an additional FePc molecule. The 1:2 adduct is unstable and decomposes slowly with oxidation of Fe(II) and the phthalocyanine ligand, via two simultaneous processes, one of which requires the intervention of a dioxygen molecule. There are no clear-cut indications, however, to state that dioxygen is also consumed in this process. The occurrence of an induction period, sometimes observed, is discussed.

Iron(II) phthalocyanine, FePc,[2] has been widely studied as a model system for heme proteins such as hemoglobin and myoglobin. Although easily accessible as a stable iron(II) species in the solid state,[3] like many other metal phthalocyanines, FePc is sparingly soluble in common nondonor solvents (solubility in water $\leq 10^{-4}$ M) and somewhat more soluble in N-donor solvents, with implied coordination of the N base at the axial sites of the central metal atom.[4] FePc and several other metal phthalocyanines dissolve appreciably (ca. 10^{-2} M) in 96% H_2SO_4,[3] probably owing to proton affinity of the outer N atoms of the phthalocyanine ring. Hence, extensive studies for these complexes have been carried out in 96% H_2SO_4 concerning methods of purifying phthalocyanines,[3] different crystal modifications,[5] protonation,[6] and interaction with small molecules.[7]

We recently described some preliminary results on the interaction of FePc with CO, NO, and O_2 in 96% H_2SO_4.[8] Interaction with CO and NO has also been dealt with elsewhere.[7,9] In our report,[8] however, it was shown for the first time that a reversible oxygenation process occurs for FePc with

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molecular oxygen, in an overall two-step process where oxygenation is followed by the irreversible oxidation of the complex molecule. In the present paper the results of a detailed kinetic study are reported and a reaction mechanism between FePc and O_2 is proposed.

Experimental Section

FePc was purchased from either Eastman Kodak Co. or Pfaltz and Bauer, Inc., and purified according to known procedures.[3] Its purity was checked by elemental analysis (C, H, N) and room-temperature magnetic moment[10] (found: $\mu_{\mathrm{eff}} = 3.87\ \mu_B$). Sulfuric acid was a Merck "Suprapur" reagent. Nitrogen and oxygen were both high-purity gases. They were also used as mixtures of suitable composition; the latter was checked by mass spectrometry.

The solubility of pure oxygen in concentrated sulfuric acid, at 20 °C, was determined by measuring directly the amount of oxygen dissolved into a known volume of acid, after a sufficiently prolonged contact. Repeated experiments gave a value of $(1.0 \pm 0.1) \times 10^{-3}$ M for the equilibrium concentration of oxygen in 96% H_2SO_4 at 20 °C and under 1.0 atm of pressure. This value is in good agreement with that found by Gubbins and Walker (1.1×10^{-3} M).[11] When sulfuric acid was allowed to equilibrate with an oxygen–nitrogen mixture under 1.0 atm of total pressure, Henry's law was assumed to hold and the oxygen concentration of the solution was calculated accordingly. Measurements of the total amount of oxygen consumed by FePc in 96% H_2SO_4 were carried out with a conventional manometric apparatus. The FePc solutions were ca. 10^{-2} M, and interaction was allowed to proceed up to complete decoloration of the solution (the time required was ca. 24 h). The final quantity of O_2 corresponded to a O_2:Fe(II) molar ratio of 0.6 ± 0.1.

Spectra of FePc solutions of different concentrations (10^{-4}–10^{-6} M in 96% H_2SO_4 and with careful exclusion of oxygen; see below) were registered at 20 °C. The solutions were found to obey closely the Lambert–Beer law and, after correction for dilution, the spectra were virtually superimposable.

Kinetic Measurements. Concentrated (usually 96% H_2SO_4) sulfuric acid was saturated with a dioxygen–dinitrogen mixture of a given composition by bubbling the gaseous mixture through the acid for at least 30 min. An aliquot (2.7 cm^3) of this solution was then poured into a 1-cm spectrophotometric cell which was then introduced into the cell compartment of a Cary 14 spectrophotometer and thermostated at 20.0 ± 0.1 °C. The cell was stoppered with a Teflon plug provided with a rubber membrane through which two platinum needles could be introduced, one of which dipped into the acid. The dioxygen–dinitrogen mixture was then bubbled into the acid for an additional 10–15 min to ensure equilibrium between the gaseous and the liquid phase inside the spectrophotometric cell. A small volume (ca. 30 μL) of an approximately 10^{-2} M N_2-saturated solution of FePc was then introduced into the cell by means of a microsyringe fitted with a platinum needle. The cell was rapidly shaken and the absorbance of the resulting solution (at 775 nm; suitably large changes in absorbance) recorded. The reference cell was filled with concentrated H_2SO_4. The concentration of oxygen was always at least 10 times larger than the concentration of FePc, the latter being ca. 10^{-5} M.

Results

In all cases the absorbance of the reaction solutions decreased rapidly and, after 5–15 min (depending on the oxygen concentration), reached a value which was nearly half of the starting absorbance. At this point the absorbance was still decreasing, albeit at a much lower rate, and several hours later it was practically zero. This behavior was taken to indicate that two consecutive reactions occur, the first being much faster than the second. Both steps could be analyzed kinetically as described below.

Very often, *but not always*, an induction period was observed. Since its occurrence was not systematic, it was attributed to interference and, hence, was not considered when analyzing the optical data for kinetic measurements. Each step of the experimental procedure was carefully checked to find the origin of this interference. Only a rough correlation was observed between the length of the induction period and the concentration of oxygen, the former increasing with decreases in the latter. A tentative explanation of the induction effect, based on this observation, is reported below.

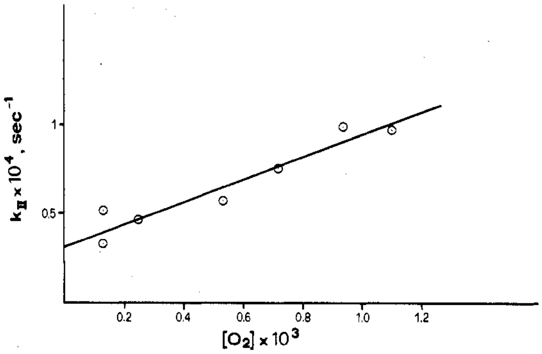

Figure 1. Step II: linear dependence of k_{II} on oxygen concentration.

The Second Step. When spectrophotometric data recorded after the first, rapid decrease of absorbance were analyzed according to the first-order law

$$\ln (D_t - D_{\infty,II}) = k_{II}t + \text{constant}$$

where D_t is the absorbance at time t and $D_{\infty,II}$ is zero, good linear plots for more than 2 half-lives were obtained. Figure 1 shows the pseudo-first-order rate constants, k_{II}, as given by least-squares analysis of the data. It appears that k_{II} depends on the concentration of oxygen according to eq 1, with $k_{II}' =$

$$k_{II} = k_{II}' + k_{II}''[O_2] \tag{1}$$

$3.2_3 \times 10^{-5}$ s^{-1} and $k_{II}'' = 6.1_2$ s^{-1} M^{-1}.

The First Step. Although the first step is much faster than the second, the two reactions partially overlap, so that it is necessary to make corrections for the second process when evaluating the rate constant of the first.

A system of two consecutive first-order reactions

$$A \xrightarrow{k_I} B \xrightarrow{k_{II}} C$$

was assumed. The optical data due essentially to the first step were treated according to a first-order kinetic law assigning an "infinite time" reading, $D_{\infty,I}$, such as to obtain the best linearity of the first-order plot. The least-squares correlation coefficient was taken as a "measure of best fitting". An approximate value of the pseudo-first-order rate constant, k_I, was thus obtained. The $D_{\infty,I}$ values estimated by this procedure were found to be a constant fraction of the zero-time absorbance, D_0, within ±5% ($D_0/D_{\infty,I} = 2.0 \pm 0.1$), independently of the rate constant, which varied, instead, in the range $(1.0–0.12) \times 10^{-2}$ s^{-1}, depending on the oxygen concentration. This fact indicates that the $D_{\infty,I}$ values chosen at this stage were not too different from the final absorbances which would have been reached had the second process been absent.

Better values for $D_{\infty,I}$ and k_I were then obtained through the following procedure. Straightforward elaboration of the well-known equations valid for a system of two consecutive first-order reactions yields eq 2 for the absorbance at a given

$$D_t = [D_{\infty,I} + (D_0 - D_{\infty,I})e^{-k_It}] + (D_{\infty,II} - D_{\infty,I})\left(1 + \frac{k_{II}e^{-k_It} - k_Ie^{-k_{II}t}}{k_I - k_{II}}\right) \tag{2}$$

time, D_t, where $D_{\infty,II}$ is the absorbance measured at the end of the second step ($D_{\infty,II} = 0$ in the present case). The sum within square brackets represents the absorbance, D_t, which would be measured at any given time were the second step absent.

The experimental data were thus treated according to eq 2, using for $D_{\infty,I}$ and k_I the approximate values estimated as described above and for k_{II} the value calculated by means of eq 1. The sets of D_t' values so obtained were then analyzed according to a first-order law. Good linearity was observed

Table I. Pseudo-First-Order Rate Constants k for the First Step[a]

$10^3[O_2]$, M	10^2k_I, s^{-1}	$10^3[O_2]$, M	10^2k_I, s^{-1}
1.10	0.98_0	0.53_2	0.53_6
	0.95_2		0.54_0
	1.01		0.51_0
	1.0_0		0.62_7[b]
	1.0_6		0.48_5
	1.0_2		av 0.51_8
	av 1.0_1		
0.93_6	0.92_2	0.24_9	0.30_2
	0.85_5		0.32_5
	0.83_0		0.29_3
	0.86_6		0.26_3
	0.88_7		0.26_0
	0.86_2		av 0.28_8
	av 0.87_0	0.12_8	0.10_1[b]
0.72_1	0.77_8[b]		0.13_4
	0.67_8		0.13_4
	0.67_5		av 0.13_4
	0.70_3	0.090_2	0.10_9
	0.69_5		0.11_3
	0.68_0		0.10_8
	av 0.68_7		av 0.11_0

[a] The temperature was 20 °C. [b] Not included in the average.

Table II. Effect of Addition of $NaHSO_4$ or H_2O on the Rate Constants k_I and k_{II}[a]

added $[NaHSO_4]$, M	added $[H_2O]$, M	10^2k_I, s^{-1}	k_{II}, s^{-1}
		0.87[b]	0.090[c]
2.2			0.17_7
2.2		1.0_7	0.17_7
	3.7	1.0_2	0.18_7
	3.7	1.0_2	0.24_0

[a] The temperature was 20 °C. A constant oxygen concentration of 0.936×10^{-3} M was maintained. [b] Average of the values reported in Table I for $[O_2] = 0.936 \times 10^{-3}$ M. [c] Calculated according to eq 1.

in all cases for at least 2 half-lives, and the pseudo-first-order rate constants calculated by least-squares analysis are reported in Table I, together with reaction conditions. The procedure described was tested on a computer-simulated set of D_t values obtained for two consecutive reactions with $k_I/k_{II} = 100$. The agreement between calculated and a priori fixed values was excellent (better than 0.2%) for both k_I and $D_{\infty,I}$.

As shown in Table I, the rate constants k_I were usually reproducible within ±5%, although, occasionally, considerably larger deviations were observed. No explanation can be given for this. The effect may be due, at least in part, to changes in bubbling (ambient) pressure, assumed to be in all cases 760 torr.

Effect of Added $NaHSO_4$ or H_2O. A few runs were carried out with the addition of either $NaHSO_4$ or H_2O to the reaction mixture. In all cases the rate of both steps was enhanced, although the increase of k_{II} was considerably higher. The results obtained are reported in Table II.

Reversibility of Steps I and II. Previous experiments showed that after reaction with oxygen for a few seconds, continuous bubbling with N_2 caused the spectrum of a 96% H_2SO_4 solution of FePc to change to the initial spectrum. By way of contrast, nitrogen bubbling was inefficient in restoring the starting spectrum when carried out several minutes after contact with O_2, i.e., after the second step had occurred to a significant extent. These observations have been confirmed. In addition, a 10^{-3} M solution of FePc was allowed to react with oxygen (10^{-3} M) for a length of time corresponding to 10 half-lives of step I. Dinitrogen was then bubbled vigorously for 10 min to eliminate the oxygen and an amount (ca. 30 μL) of solution was injected into a spectrophotometric cell containing oxygen-free H_2SO_4 equilibrated with nitrogen. The absorbance at 775 nm was then recorded and was shown to increase slowly. After ca. 3 h the absorbance reached a maximum and then started to decrease. If nitrogen was not bubbled after reaction with oxygen (so that the solution after dilution with oxygen-free H_2SO_4 did contain a small concentration of oxygen), the absorbance started to decrease immediately. All of these facts confirm that step I is reversible while step II is not. Moreover, the concentration of oxygen sufficient to inhibit reversibility of step I is very low, being of the same order of magnitude as the concentration of FePc (ca. 10^{-5}–10^{-6} M).

Discussion and Conclusions

The Nature of FePc in H_2SO_4 Solution. Although the molecular structure of FePc in the solid state is well-known,[13] the nature of the species present in a concentrated sulfuric acid solution is not obvious. An extensive investigation on several metal phthalocyanines has led Berezin[6a] to suggest the occurrence in that medium of a monoprotonated species of general formula $MPcH^+$ (M is a bivalent transition- or non-transition-metal atom). More recently, however, tetraprotonation, with protons localized on the outer N atoms of the phthalocyanine ring, has been suggested for free phthalocyanine and its Cu(II) derivative in chlorosulfuric acid.[6c] It has been also shown that CuPc undergoes several protonation equilibria in H_2O–H_2SO_4 solutions and that a tetraprotonated species is formed in 96% H_2SO_4.[6b] Since changing Cu(II) by Fe(II) should have no appreciable effect on the Lewis-base properties of the outer N atoms of the phthalocyanine molecule, there should be no difficulty in assigning the same degree of protonation also for FePc, as has in fact been done in a report concerning the interaction of FePc with CO in 96% H_2SO_4.[7]

The tendency of the central metal ion to reach hexacoordination through interaction along the axial directions with the solvent molecules has been known since FePc was described for the first time.[3,4b] In a medium such as 96% H_2SO_4, where large concentrations of negative ions are present, i.e., HSO_4^- (ca. 4 M), the tetraprotonated species $FePcH_4^{4+}$ will also carry coordinated ions along the fifth and sixth coordination positions of Fe(II).

A monomer–dimer equilibrium seems to have been observed in an aprotic solvent (Me_2SO) for FePc.[14] However, the existence of an appreciable monomer–dimer equilibrium in 96% H_2SO_4 and under present concentration conditions is unlikely. In fact, the spectrum of FePc solutions was found to remain unchanged upon dilution (see Experimental Section). Furthermore, association between positively multicharged (4+) species seems to be hardly acceptable.

Reaction with Oxygen. Previous[8] and present experiments show that FePc combines reversibly with oxygen in concentrated sulfuric acid (step I) giving a species which, in turn, decomposes irreversibly (step II) with formation of Fe(III) and oxidation of the phthalocyanine macrocycle. Attempts were made to isolate and characterize the final products of both steps. However, they were unsuccessful, mainly for reasons which depend on the peculiar properties of the solvent. As mentioned previously,[8] the only isolable product was phthalimide, obtained upon addition of water to the reaction mixture at the end of the irreversible step.

Despite the lack of direct information on the nature of the compounds involved, we believe that the present kinetic study allows a reasonable reaction scheme to be proposed.

When the rate constant k_I is plotted vs. the concentration of oxygen, the plot of Figure 2 is obtained. Although a reasonable zero-intercept line can be drawn through most of the experimental points, the best fit is obtained with the dashed curve in the figure. Kinetic measurements at oxygen con-

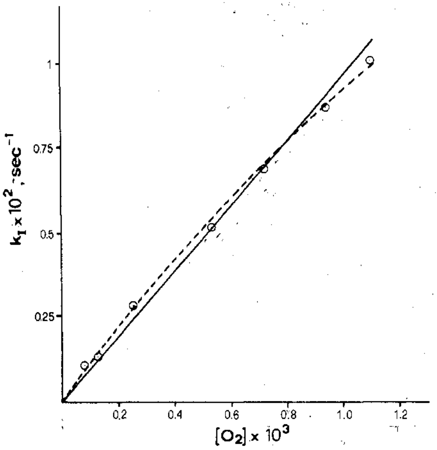

Figure 2. Step I: pseudo-first-order rate constant k_I as a function of oxygen concentration.

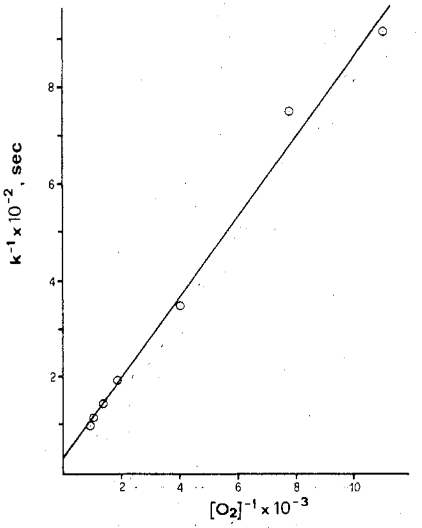

Figure 3. Linear plot of k_I^{-1} vs. $[O_2]^{-1}$.

centrations higher than 1.1×10^{-3} M (i.e., at O_2 pressures higher than 1 atm) have not been tried and thus a more clear-cut choice is not possible. However, there is no reason to believe that the departure from linearity, albeit not very large, is fortuitous. We, thus, assume that the curvature is real and is related to the reaction mechanism.

Figure 3 shows the plot of k_I^{-1} vs. $[O_2]^{-1}$. The fairly linear trend with nonzero intercept suggests eq 3. Least-squares analysis yields for a and b the values of 12.1 s^{-1} M^{-1} and 3.92×10^2 M^{-1}, respectively.

$$k_I = a[O_2]/(1 + b[O_2]) \tag{3}$$

The reversible reaction between oxygen and iron(II) porphyrins has been widely studied[15] and is still a stimulating research field due to its obvious implications for biological systems. As the final product of the reversible oxygenation, a 1:1 O_2 adduct forms, which may react with excess iron(II) porphyrin yielding a bridged $Fe^{II}–O_2–Fe^{II}$ complex, the latter being generally unstable toward oxidation to Fe(III). Interaction with oxygen has been studied for the water-soluble tetrasulfonated cobalt(II) and iron(II) phthalocyanines.[16] For FePc itself only indications of an interaction with oxygen were reported,[17] but no systematic investigations have been carried out. In agreement with previous findings on the above-cited, closely related systems,[15] present results are consistent with the mechanism

$$S_2FePc \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SFePc + S \tag{4}$$

$$SFePc + O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} SFePcO_2 \tag{5}$$

$$SFePcO_2 + SFePc \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} SFePcO_2FePcS \tag{6}$$

where S is HSO_4^- and charges are omitted for simplicity.

Reversibility experiments showed that even trace amounts of oxygen are sufficient to prevent reobtainment of the starting substrate, and even under vigorous nitrogen bubbling the change to the initial spectrum is slow. This requires that both k_{-2} and k_{-3} are small. Moreover, if both intermediates SFePc and $SFePcO_2$ are very reactive (i.e., $k_2[O_2]$ and k_3 are very large), steady-state conditions may be applied, leading to the rate equation

$$\frac{d[S_2FePc]}{dt} = \frac{-2k_1k_2[O_2]}{k_{-1}[S] + 2k_2[O_2]}[S_2FePc] \tag{7}$$

for step I, and, hence

$$k_I = 2k_1k_2[O_2]/(k_{-1}[S] + 2k_2[O_2]) \tag{8}$$

Equation 8 is equivalent to eq 3 with $a = 2k_1k_2/k_{-1}[S]$ and $b = 2k_2/k_{-1}[S]$. From the ratio a/b, $k_1 = a/b = 3.08 \times 10^{-2}$ s^{-1} is obtained, and taking the value of 4.1 M for $[HSO_4^-]$ (corresponding to the formal concentration of water in 96% H_2SO_4), we estimate the ratio k_2/k_{-1}, which measures the selectivity of the pentacoordinate intermediate toward the incoming nucleophiles O_2 and HSO_4^-, to be ca. 800. There are relatively few systems with which the present results may be compared, because of the nature of both solvent and inert axial ligand. It can only be said that the rate constant for generating the pentacoordinate intermediate falls in a reasonable range, being not too dissimilar to the rate constant of base or CO release of $(base)_2FePc$ and (base)FePcCO complexes at 23 °C in toluene (base = imidazole, piperidine, pyridine).[18] The discrimination factor k_2/k_{-1} is remarkably higher when compared with that shown by the pentacoordinate intermediates (base)FePc toward CO and base. In these cases CO is slightly unfavored with respect to base (base = imidazole, piperidine, pyridine, 2-methylimidazole), but the ratio k_2/k_{-1} remains close to unity ($k_2/k_{-1} \approx 0.25$ on the average).

In the case of iron(II) porphyrins it has been suggested that large discrimination in favor of entering groups of small size might be related to the out-of-plane position of the Fe atom in the high-spin pentacoordinate intermediate, this geometry making difficult the interaction with a bulk nucleophile.[18] Such an argument, however, is unlikely to apply to the present case. The low basicity and the low π-bonding character of the HSO_4^- ion might be a better explanation for the observed discrimination.

Equation 8 suggests that an increase of HSO_4^- concentration should cause a decrease of k_I. Experiments have been carried out in which HSO_4^- was increased by adding either $NaHSO_4$ or H_2O. The results, shown in Table II, do not agree with this prediction, since a 20% increase is observed instead of an expected 30–40% decrease. However, it is possible that changes in the properties of the medium are responsible for compensating effects. For example, addition of water decreases the acidity of the medium[19] and this may influence the extent of protonation of the substrate.[6b]

As an alternative to the proposed mechanism, Fe(II) could be considered as essentially tetracoordinate in the starting FePc, and eq 1 could be replaced by eq 9 in the reaction scheme

$$FePc + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SFePc \tag{9}$$

Equation 8 would then become

$$k_{\mathrm{I}} = 2k_1k_2[\mathrm{S}][\mathrm{O}_2]/(k_{-1} + 2k_2[\mathrm{O}_2]) \qquad (10)$$

Equation 10 does predict an increase of k_{I} with increasing $[\mathrm{HSO_4^-}]$. However, in view of the above considerations on the nature of the substrate species, the tetracoordination about iron(II) does not seem reasonable.

The species $\mathrm{SFePcO_2FePcS}$ formed via eq 6 is unstable and decomposes irreversibly, giving species which do not absorb in the range 500–900 nm. No systematic efforts have been made to identify the reaction products, but there is little doubt that iron(III) is formed. Also, phthalimide has been isolated from the reaction solution after addition of water.

The two-term rate equation (eq 1) which describes step II suggests the existence of two simultaneous decomposition pathways for the 2:1 $\mathrm{Fe(II)\cdot O_2}$ adduct, one of which requires the intervention of 1 mol of oxygen. The overall consumption of oxygen at the end of step II (0.6 ± 0.1 mol of $\mathrm{O_2}$/mol of FePc), as measured here, seems to suggest that only step I does involve oxygen uptake, the amount left for the second step (≤0.2 mol/mol of FePc) being of the same order of magnitude as the experimental errors. However, oxygen-uptake experiments (see Experimental Section) were carried out under heterogeneous conditions (i.e., with a gas-phase–solution-phase equilibrium involved), and the actual concentration of dioxygen in solution was not known. Hence, the relative contributions of k_{II}' and k_{II}'' pathways cannot be assigned.

Induction Period. As stated above (see Experimental Section), after mixing, the absorbance of the reacting solutions sometimes remained nearly constant or tended to decrease with progressively steep slopes. The occurrence and the features of this induction phenomenon were not predictable and sometimes it was totally absent. This fact and the observed (roughly) inverse correlation of the induction period with the concentration of oxygen might suggest that the intermediate $\mathrm{SFePcO_2}$ reacts with some reducing impurities, X, giving back the starting substrate, i.e.

$$\mathrm{SFePcO_2} + \mathrm{X} \xrightarrow{k_{\mathrm{X}}} \mathrm{SFePc} + \text{oxidation products} \qquad (11)$$

In the limiting case $k_{\mathrm{X}} >> k_3$ the absorbance should remain essentially constant as long as a significant amount of X is present. It is easy to show, under steady-state conditions for SFePc and $\mathrm{SFePcO_2}$ and with neglect of eq 6 ($k_{\mathrm{X}} >> k_3$), that

$$\mathrm{d}[\mathrm{X}]/\mathrm{d}t = -k_1k_2[\mathrm{Fe(II)}][\mathrm{O_2}]/(k_{-1}[\mathrm{HSO_4^-}])$$

Since all concentrations involved (except [X]) do not change appreciably during the induction period, the latter may be calculated as

$$\Delta t_{\mathrm{ind}} = k_{-1}[\mathrm{HSO_4^-}][\mathrm{X}]_0/(k_1k_2[\mathrm{Fe(II)}][\mathrm{O_2}])$$

where $[\mathrm{X}]_0$ represents the initial concentration of reducing impurities. The above equation predicts that Δt_{ind} is inversely proportional to the concentration of oxygen, as observed.

Registry No. $\mathrm{S_2FePc}$, 68813-18-3; $\mathrm{O_2}$, 7782-44-7.

References and Notes

(1) Istituto di Chimica Generale ed Inorganica, Università di Roma, Roma, Italy.

(2) Pc is the dianion of phthalocyanine.

(3) P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1719 (1936).

(4) (a) J. S. Anderson, E. F. Bradbrook, A. H. Cook, and R. P. Linstead, *J. Chem. Soc.*, 1151 (1938); (b) P. A. Barrett, D. A. Frye, and R. P. Linstead, *ibid.*, 1157 (1938).

(5) M. T. Robinson and G. E. Klein, *J. Am. Chem. Soc.*, **74**, 6294 (1952); F. W. Karasek and J. C. Decius, *ibid.*, **74**, 4716 (1952); C. Ercolani, C. Neri, and P. Porta, *Inorg. Chim. Acta*, **1**, 415 (1967).

(6) (a) B. D. Berezin, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **2**, 165 (1959); (b) S. Gaspard, M. Verdaguer, and R. Viovy, *J. Chim. Phys.*, 1740 (1972); (c) D. L. Ledson and M. V. Twigg, *Inorg. Chim. Acta*, **13**, 43 (1975).

(7) S. Gaspard, R. Viovy, J. M. Bregeault, C. Jarjour, and S. Yolou, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **281**, 925 (1975).

(8) I. Collamati, C. Ercolani, and G. Rossi, *Inorg. Nucl. Chem. Lett.*, **12**, 799 (1976).

(9) C. Ercolani, C. Neri, and G. Sartori, *J. Chem. Soc. A*, 2123 (1968), and references therein.

(10) H. Senff and W. Klemm, *J. Prakt. Chem.*, **154**, 73 (1939); A. B. P. Lever, *J. Chem. Soc.*, 1821 (1965).

(11) K. E. Gubbins and R. D. Walker, Jr., *J. Electrochem. Soc.*, **112**, 469 (1965).

(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2nd ed., Wiley, New York, London, 1961, p 166.

(13) J. M. Robertson, *J. Chem. Soc.*, 615 (1935); R. P. Linstead and J. M. Robertson, *ibid.*, 1736 (1936); J. F. Kirner, W. Dow, and W. R. Scheidt, *Inorg. Chem.*, **15**, 1685 (1976).

(14) J. G. Jones and M. V. Twigg, *Inorg. Nucl. Chem. Lett.*, **8**, 305 (1972).

(15) J. E. Baldwin and J. Huff, *J. Am. Chem. Soc.*, **95**, 5757 (1973); J. P. Collmann, R. R. Gagne, T. R. Halbert, J.-C. Marchon, and C. A. Reed, *J. Am. Chem. Soc.*, **95**, 7868 (1973); W. S. Briniger, C. K. Chang, *ibid.*, **96**, 5595 (1974); W. S. Briniger, C. K. Chang, J. Geigel, and T. G. Traylor, *ibid.*, **96**, 5597 (1974); D. L. Anderson, C. J. Weschler, and F. Basolo, *ibid.*, **96**, 5599 (1974); J. Almog, J. E. Baldwin, R. L. Dyer, J. Huff, and C. J. Wilkerson, *ibid.*, **96**, 5600 (1974); J. Almog, J. E. Baldwin, and J. Huff, *ibid.*, **97**, 227 (1975); C. J. Weschler, D. L. Anderson, and F. Basolo, *ibid.*, **97**, 6707 (1975); E. Tsuchida, K. Honda, and H. Sata, *Inorg. Chem.*, **15**, 352 (1976).

(16) D. Vonderschmitt, K. Bernauer, and S. Fallab, *Helv. Chim. Acta*, **48**, 951 (1965); J. H. Weber and D. H. Busch, *Inorg. Chem.*, **4**, 469 (1965); E. W. Abel, J. M. Pratt, and R. Whelan, *Chem. Commun.*, 449 (1971); L. C. Gruen and R. J. Blagrove, *Aust. J. Chem.*, **26**, 319 (1973); D. M. Wagnerova, E. Schwertnerova, and J. Veprek-Siska, *Collect. Czech. Chem. Commun.*, **39**, 1980 (1974); H. Przywarska-Boniecka and K. Fried, *Rocz. Chem.*, **50**, 43 (1976); H. Przywarska-Boniecka, L. Trynda, and E. Antonini, *Eur. J. Biochem.*, **52**, 567 (1975); G. McLendon, and A. E. Martell, *Inorg. Chem.*, **16**, 1812 (1977).

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

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

(19) G. Charlot and B. Trémillon, "Les Réactions Chimiques dans les Solvants et les Sels Fondus", Gauthier-Villars, Paris, 1963, p 245.