

Kinetics of Autoreduction of Iron(III) Porphyrins by Cyanide Ion

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Abstract

The autoreduction of ferric porphyrins in the presence of cyanide ions in dimethyl sulfoxide (DMSO) is followed by visible spectroscopy. The presence of an isosbestic point during autoreduction from iron(III) to iron(II) porphyrins suggests it to be an equilibrium process. The observed rate of reduction was found to be linearly dependent on the concentration of cyanide ion. The rate constants calculated for three iron porphyrins viz. tetraphenylporphyrin iron(III), deuteroporphyrin dimethyl ester iron(III) and octaethyl porphyrin iron(III) are 240, 165 and 120 $\text{M}^{-1}\text{s}^{-1}$, respectively. The rate constants are found to increase with a decrease in the basicity of the porphyrin. Based on these observations, a nucleophilic attack mechanism is proposed which explains the linear dependence of the observed rate.

Introduction

Ferric porphyrins undergo autoreduction in the presence of potential ligands, such as piperidine [1], cyanide [2, 3], n-hexanethiol [3] and phosphine [3]. Recently hydroxyl ion has been shown to induce reduction of ferric porphyrin in pyridine [4] and DMSO [5] solutions. Iron porphyrins are present as the prosthetic group in heme proteins. Understanding of the mechanisms of one-electron transfer in such model systems is very important because heme proteins in biological systems are involved in one-valency changes as for example in peroxidases [6] and cytochromes [7].

Among the reactions of the various potential ligands studied so far, the autoreduction of cyanoferriporphyrins has been studied by Del and La Mar [2, 3]. Based on NMR and EPR studies the authors proposed a mechanism which involves intramolecular one-electron transfer by homolytic cleavage of the Fe–CN bond. They did not, however, define the role of cyanide ion concentration although $[\text{CN}^-]$ clearly affected the rate of reduction. In the presence of 20 to 100 fold excess of cyanide

equivalents and because of the formation of the cyanide tetramer radical ion, they proposed a very complex dependence of the rate of reduction on cyanide ion concentration. We report herein our kinetic studies on the reduction of cyanoferriporphyrins in DMSO using the spectrophotometric method. The purpose of these studies was to evaluate quantitatively the dependence of the rate of reduction on the cyanide ion concentration, deduce the rate constant and to propose a mechanism of reduction consistent with the observed rate law.

Experimental

Tetraphenyl porphyrin (TPP) was synthesized and purified by the literature method [8]. Octaethyl porphyrin (OEP) and deuteroporphyrin dimethyl ester (DPDME) were obtained from Sigma and were metalated using the standard procedure [9]. KCN (May and Baker) was used without further purification. Dimethyl sulfoxide (DMSO) was deoxygenated by several freeze–thaw–pump cycles and was stored under nitrogen. All the samples were prepared in nitrogen atmosphere.

Visible spectral were recorded on a Cary-17D spectrophotometer at $22 \pm 0.2^\circ\text{C}$. The porphyrin solution in DMSO (10^{-6} to 10^{-5} M) was placed in a cuvette and was sealed using a rubber septum. The cuvette was then taken out of the glove box and placed in the sample cavity. The cyanide solution in DMSO was introduced in the cuvette using a Hamilton syringe and spectra were recorded at regular intervals. For determination of the rate constants, absorption at Soret maxima (~ 400 nm) for various species were monitored.

Results and Discussion

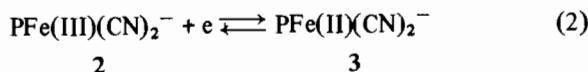
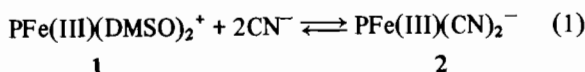
Addition of cyanide to a solution of ferric porphyrin in DMSO produces low-spin ferric porphyrin bis-cyanide [2]. This complex then undergoes autoreduction to ferrous bis-cyanide species [2, 3].

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TABLE 1. Soret band maxima of PFe(III)(DMSO)₂, PFe(III)(CN)₂ and PFe(II)(CN)₂ in DMSO and the rate constants for the autoreduction of PFe(III)(CN)₂ to PFe(II)(CN)₂ in DMSO at 22 °C^a

Porphyrin	λ_{\max}^b (nm)			<i>K</i> (M ⁻¹ s ⁻¹)
	PFe(III)(DMSO) ₂	PFe(III)(CN) ₂	PFe(II)(CN) ₂	
TPP	412	419	434	240
OEP	394	406	424	120
DPDME	390	404	420	165

^aAbbreviations: DMSO = dimethyl sulfoxide, TPP = tetraphenyl porphyrin, OEP = octaethyl porphyrin, DPDME = deuteroporphyrin dimethyl ester. ^b± 1 nm.



P = porphyrin

Each species has a characteristic absorption spectrum and a distinct Soret band, Table 1. During autoreduction of 2 to 3 the Soret band intensity of 2 decreases in the course of time to give a new Soret band maxima characteristic of species 3. The time dependent decrease in Soret band absorption was found to be exponential. Thus the rate constant can be evaluated by monitoring changes in absorbance at Soret band maxima of species 2. TPPFe(III)(DMSO)₂ has Soret maxima at 412 nm. When a solution of KCN in DMSO is added to this, ferric bis-cyanide is formed with Soret absorption at 419–420 nm. The ferric bis-cyanide slowly autoreduces to ferrous bis-cyanide having Soret maxima at 434 nm. Thus the progress of autoreduction may be followed at 419 nm, i.e. rate of disappearance of ferric species or at 434 nm, i.e. rate of formation of ferrous species. Figure 1 shows spectra recorded during the course of autoreduction at regular intervals. The presence of a clear isosbestic point indicates that the conversion of ferric bis-cyanide to ferrous bis-cyanide is an equilibrium process. Figure 2 shows the course of autoreduction followed at 419 nm with time. In Fig. 3 $\ln A$ is plotted as a function of time, giving a straight line. Experiments were performed keeping the porphyrin concentration constant and increasing the cyanide concentration from 2 to 20 fold excess. Figure 3 shows the plots of $\ln A$ as a function of time for various concentrations of cyanide. It is evident from Fig. 3 that the observed rate of reduction strongly depends on the cyanide ion concentration. The rate increases with increase in cyanide concentration. Since we are taking cyanide concentration in excess, the rate law followed by the reaction is given by

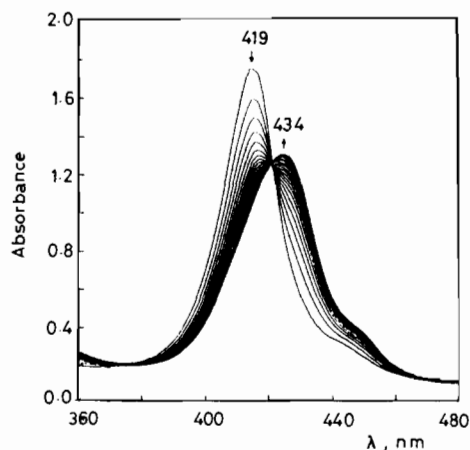


Fig. 1. Spectral changes occurring during autoreduction of TPPFe(III)(CN)₂ to TPPFe(II)(CN)₂ in DMSO at 22 °C. [P] = 1.15 × 10⁻⁵ M, [CN⁻] = 4.13 × 10⁻⁵ M.

$$\frac{-d[\text{PFe(III)(CN)}_2^{1-}]}{dt} = K_{\text{obs}}[\text{PFe(III)(CN)}_2^{1-}]$$

where $K_{\text{obs}} = K[\text{CN}^-]$

We observe in this case that K_{obs} varies linearly with the cyanide concentration employed in our studies (2 to 20 fold excess, Fig. 3). Reduction of metalloporphyrins using exogenous reducing agents such as Cr(II), Ru(II) and V(II) has been studied by several workers [10–14]. In most of the kinetic studies reported, K_{obs} was found to vary linearly with the concentration of the reducing agent employed. Figure 4 shows the linear dependence of K_{obs} on cyanide ion concentration in the autoreduction of TPPFe(III)(CN)₂ to TPPFe(II)(CN)₂ in the present case. The slope of the line now gives the rate constant 'K' which is 240 M⁻¹ s⁻¹.

Cyanide ion itself is not known to be a reducing agent. The observed linear dependence therefore suggests that it is mechanistically involved in the ferric ion reduction. A nucleophilic attack on the coordinated ferric ion by free CN⁻ present in the solution may initiate homolytic cleavage of the

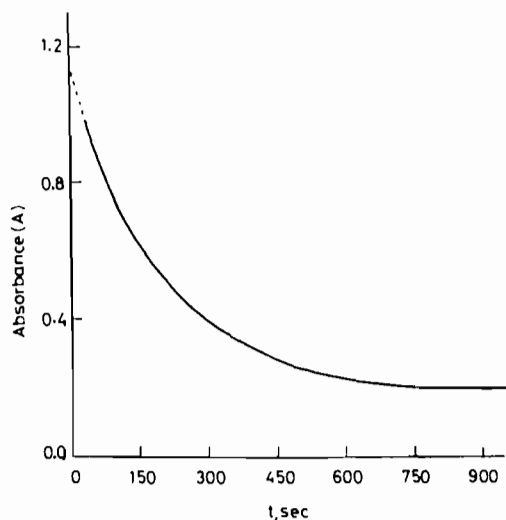


Fig. 2. Experimental trace of absorbance at 419 nm vs. time for autoreduction of TPPFe(III)(CN)₂ to TPPFe(II)(CN)₂. Concentration as in Fig. 1.

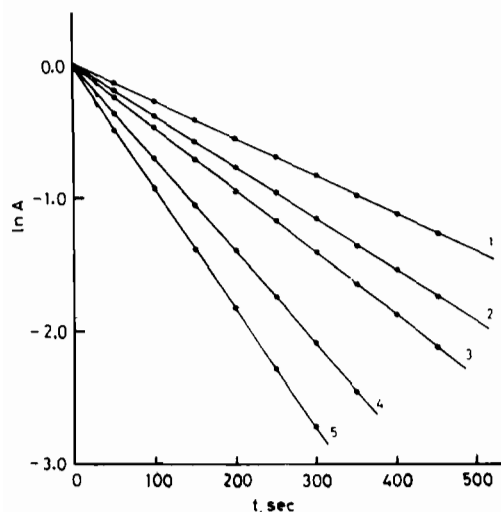


Fig. 3. Plots of $\ln A$ vs. time for autoreduction in Fig. 2 for various concentration of cyanide: 1, 2.27; 2, 3.43; 3, 4.13; 4, 4.43; 5, 5.50×10^{-5} M.

leaving cyanide group (Scheme 1) producing an electron in the close vicinity of ferric ion and thereby reducing it to the Fe(II) valency state. The cyanide radical produced may combine with another such radical to give (CN)₂ species. This mechanism is consistent with the observed linear dependence of K_{obs} on $[\text{CN}^-]$, in that the concentration of the reducing electron produced during homolytic cleavage is directly proportional to the cyanide concentration. All our attempts to detect cyanide tetramer radical as observed by Del and La Mar [2, 3] failed. We therefore feel that formation of the tetramer radical ion in the concentration range employed here $\sim 10^{-4}$ – 10^{-5} M is most unlikely

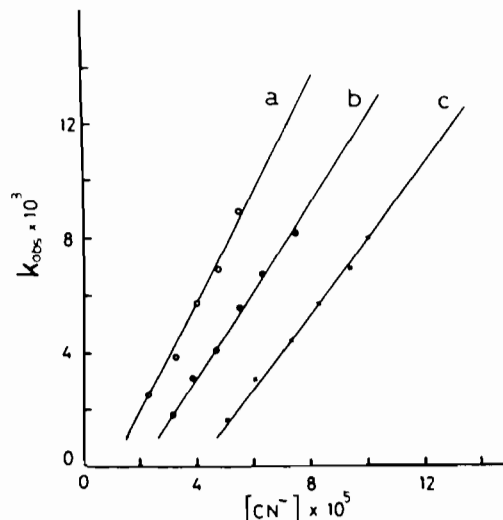
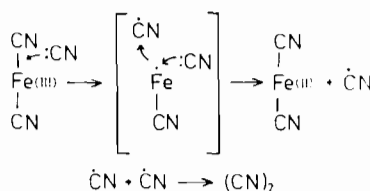


Fig. 4. Plots of K_{obs} vs. cyanide concentration for a, TPP; b, OEP; c, DPDME at 22 °C. Solvent: DMSO.



Scheme 1.

(concentrations used by Del and La Mar were much higher 0.1 to 0.4 M). Thus the above observations strongly suggest a nucleophilic attack mechanism operative in this concentration range.

Nucleophilic attack by cyanide ion also depends on the electrophilicity of the central ferric ion. Thus a more basic porphyrin is expected to place more electron density at the metal centre thus making it less susceptible to nucleophilic attack compared to the less basic porphyrin [15]. The basicity of the porphyrins increases in the order TPP < DPDME < OEP. The rate constants for the autoreduction of Fe(III) to Fe(II) in the above porphyrins (DPDME and OEP) determined by a similar procedure follow the order $K_{\text{OEP}} < K_{\text{DPDME}} < K_{\text{TPP}}$ (Table 1) which is consistent with the mechanism involving nucleophilic attack by cyanide ion.

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