Inorganica Chimica Acta, *179* (1991) 25–33

The electrochemistry and spectroelectrochemistry of sulfate complexes of iron porphyrins

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(Received July 19, 1990)

Abstract

The spectroscopy and electrochemistry of $[Fe(TPP)]_2SO_4$ and $[Fe(OEP)]_2SO_4$ in methylene chloride, dimethylformamide and dimethyl sulfoxide was examined. In methylene chloride, the reduction of iron(III) to iron(II) porphyrins occurs in two well-separated reduction waves. The first wave corresponds to the reduction of the sulfate-bridged dimer to Fe(P) and $Fe(P)(SO_4)^-$, where P=TPP or OEP. The second wave corresponds to the reduction of $Fe(P)(SO_4)^-$ to Fe(P). The reduction of Fe(P) occurs at the normal potential for the iron(II)/iron(I) porphyrin reduction. These results were confirmed by visible spectroelectrochemistry, proton NMR and EPR spectroscopy. In coordinating solvents such as DMF or DMSO, the sulfate-bridged dimer dissociated and a single iron(III)/iron(II) wave was observed. The addition of sulfate to the sulfate-bridged complex in methylene chloride or chloroform lead to the dissociation of the complex into the sulfate monomer complexes. The NMR spectrum of $Fe(TPP)(SO_4)^-$ was typical of a high-spin ferric porphyrin complex, and was almost indistinguishable from Fe(TPP)Cl. In the presence of excess sulfate, only one iron(III)/iron(II) wave was observed, and this wave occurred at the potential of the second wave for the sulfate-bridged dimer. As with the dimer itself, this wave was quite quasi-reversible, and the reduction wave occurred substantially negative of the iron(III)/iron(II) wave for Fe(TPP)Cl. The spectroelectrochemistry of the reduced product was consistent with a $Fe(II)(TPP)(SO_4)^{2-}$ complex. The strong complex between sulfate and iron(II) is probably due to the poor solvation of sulfate in these organic solvents. In DMSO, the results were similar to methylene chloride, except that there was no evidence for complexation of sulfate with the ferrous species. In addition to the sulfate complex, the bisulfate complex of ferric OEP was also examined, as well as the reaction of bisulfate with $Fe(TPP)(ClO_4)$. The infrared, visible and NMR spectra for $Fe(OEP)(HSO_4)$ were obtained.

Introduction

Over the past two decades, iron(III) porphyrin complexes of anions, formed from a large number of weak and strong acids, have been synthesized and characterized. One such dianion, sulfate, reacts with ferric porphyrins to form an iron-porphyrin dimer which is bridged by sulfate. The structure of this dimer has been examined by visible, EPR and NMR spectroscopy [1, 2], and its X-ray structure has been determined [3, 4]. The sulfate-bridged dimer exists as a high-spin ($S=5/2$) complex with no pairing of the spins between the irons of the dimer. The visible and NMR spectra of the sulfate dimer in non-coordinating solvents such as methylene chloride are quite similar to other high-spin ferric porphyrin complexes. However, no EPR spectrum can be observed due to the fast relaxation caused by the close proximity of the iron atoms [1, 2]. From the X-ray structure, it was found that the sulfato ligand bridges the two iron atoms in a monodentate fashion [3]. In addition to the dimeric species, the structure of a hydrogen sulfate iron porphyrin was recently reported [5]. This complex is a monomer in which hydrogen bonding was observed in the crystal structure between the coordinated hydrogen sulfate groups.

While the structure and spectroscopy of the sulfate-bridged dimer have been determined, the reactions and equilibria of this complex have not been examined in detail. Cyclic voltammetry of the sulfate-bridged dimer showed three waves with peak potentials of −0.24, −0.58 and −1.04 V versus SCE in methylene chloride [2]. The first and third waves were at potentials that corresponded to the ferric/ferrous and Fe(II)/Fe(I) waves, respectively. The voltammetric behavior of this complex was not further investigated.

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0020-1693/91/$3.50

In addition, the association/dissociation equilibria of the bridged dimer was not studied in coordinating solvents nor in the presence of excess ligand. Therefore, it will be the aim of this report to study the electrochemical and spectroscopic behavior of the sulfate-bridged dimer in order to characterize the equilibria, and to understand its stability as a function of solvent strength, redox state, and concentration of sulfate. In addition to the sulfate complex, the reaction of hydrogen sulfate with iron porphyrins will also be examined.

Experimental

Materials

Tetraphenylporphyrin (H_2TPP), octaethylporphyrinatoiron(III) chloride (Fe(OEP)(Cl)), bis(triphenylphosphoranylidene)ammonium chloride ((PNP)Cl), chloroform, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dichloromethane, and deuterated NMR solvents were purchased from Aldrich Chemical Co. in the highest purity available. Dichloromethane was purified by distillation over calcium hydride. All other solvents were used without further purification. Tetrabutylammonium perchlorate (TBAP) was obtained from G. F. Smith Chemical Co. Tetrabutylammonium tetrahydridoborate ((TBA)(BH_4)) was purchased from Alfa Products. Sodium sulfate was obtained from Mallinckrodt, Inc.

Bis[(tetraphenylporphyrinato)iron(III)] sulfate [1, 2], tetraphenylporphyrinatoiron(III) chloride and Fe(TPP)(ClO_4) [6] were synthesized by literature procedures.

Bis(triphenylphosphoranylidene)ammonium sulfate [$(PNP)_2SO_4$] was prepared by the metathesis reaction of (PNP)Cl and sodium sulfate in water [7]. The product exhibited distinctive infrared bands corresponding closely to those of sulfate ion [8]. Octaethylporphyrinatoiron(III) hydrogen sulfate, Fe(OEP)(HSO_4), was isolated, after acid hydrolysis of the μ-oxo complex with sulfuric acid, by crystallization from methylene chloride/heptane. *Anal.* Calc. for $C_{36}H_{45}FeN_4O_4S$: C, 63.06; H, 6.61; Fe, 8.14; N, 8.17; S, 4.68. Found: C, 62.75; H, 6.61; Fe, 7.70; N, 7.92; S, 4.15% (mole ratio Fe/S = 1.07/1.00).

Methods

Cyclic voltammetric and spectroelectrochemical data were obtained with either an ECO 553 potentiostat with an EG&G Princeton Applied Research (PARC) 175 waveform generator or an IBM EC/225 voltammetric analyzer. Voltammetric data were recorded on a Hewlett-Packard 7045A X-Y recorder. Scan rates ranged from 20 to 200 mV/s. A three electrode IBM cell was used for all experiments, consisting of Sargent–Welch platinum flag electrodes as the working and auxiliary electrodes, and a Ag/$AgNO_3$ (0.1 M in acetonitrile) reference electrode (SRE). The reference electrode was separated from the electrochemical solution by a salt bridge (0.1 M supporting electrolyte with the appropriate solvent) and a separator which was either an asbestos plug or a porous Vycor tip. All solutions were deoxygenated for 15 min with prepurified dinitrogen. During the measurements, a blanket of nitrogen was maintained over the solution, and, in the case of methylene chloride, the dinitrogen was saturated with the solvent. The half-wave potentials ($E_{1/2}$) were measured as the average of the anodic and cathodic peak potentials. An optically transparent thin layer electrode (OTTLE) cell, as described in ref. 9, was used for the spectroelectrochemical studies. The visible spectra were obtained following controlled potential electrolysis at the desired potential.

All visible spectra including the spectroelectrochemical data were obtained on a Perkin-Elmer 320 UV–Vis spectrophotometer with a Perkin-Elmer 3600 data station. Besides the OTTLE cell, 1 mm and 1 cm cells were used. The Soret region was obtained with the 1 mm cell while the long wavelength (450–800 nm) region was obtained with a 1 cm cell. The NMR spectra were obtained with a 60 MHz (proton) JEOL FX60Q Fourier transform NMR spectrometer or a 250 MHz Bruker NMR. The infrared spectra were obtained on an Analect FX-6200 FT infrared spectrometer. Solid infrared samples were prepared as KBr pellets. Solution infrared spectra were obtained using a 0.1 mm NaCl liquid cell (Wilmad Glass Co.). Magnetic susceptibility measurements were made using the Evans method [10, 11]. The EPR spectra were obtained on a Varian E-line Century Series EPR spectrometer.

Iron(II) porphyrins were generated from the ferric complex with either (TBA)(BH_4) or zinc amalgam [12, 13]. In the latter case, the porphyrin complex and the zinc amalgam were stirred in toluene overnight. Prior to obtaining the spectroscopic measurements, the solutions were diluted 1 to 10 in methylene chloride. In all cases, the chemical reductions were performed under an argon atmosphere in a glove box.

Results

Visible, infrared and NMR spectroscopy of [Fe(P)]$_2$(SO_4)

The proton NMR and visible spectra of the sulfate-bridged dimer in chloroform as well as its infrared

TABLE 1. Visible spectra of neutral and cationic ferric porphyrins

Complex	Solvent	Soret[a] (nm)	Other visible bands[a] (nm)	Reference
$Fe(OEP)(HSO_4)$	$CHCl_3$	382(77.9)	504(7.8), 530s, 636(4.0)	this work
$Fe(OEP)(ClO_4)$	CH_2Cl_2	380(113)	500(9.2), 633(3.2)	14
$[Fe(TPP)]_2(SO_4)$	CH_2Cl_2	406(61)	505(6.9), 569(2.7), 644(1.6), 678(1.5)	
	DMF	398(93)	501(8.2), 530(10.6), 693(4.3)	this work
	DMSO	416(66)	490(9.1), 527(7.8), 570s, 680s	this work
$Fe(TPP)^+$	DMF	409(97.3)	529(11.7), 695(2.1)	15
	DMSO	395s, 413(110)	493(11), 527(14), 640s, 686(3)	this work

[a] ϵ in parentheses, cm^{-1} mM^{-1}.

spectrum have previously been reported [1, 2]. The NMR spectra were quite similar to other high-spin ferric porphyrin spectra with the pyrrole resonance at 71.6 ppm, and the phenyl resonances at 6.53, 11.2 and 12.7 ppm. The proton NMR spectra in DMF and DMSO, though, were more complex. Additional resonances were seen for both the pyrrole and phenyl protons. The larger pyrrole resonance was observed at 68.1 ppm in DMF (74.1 ppm in DMSO), while a smaller resonance was seen at 82.8 ppm (84.2 ppm in DMSO). Similarly, the stronger phenyl resonances were observed at 13.8, 10.0 and 6.74 ppm in DMF (12.9 and 9.84 ppm in DMSO). The visible spectra for $[Fe(TPP)]_2(SO_4)$ in chloroform, methylene chloride, DMF and DMSO were similar to other high-spin ferric–TPP complexes in those same solvents (Table 1) [1, 2]. Care needed to be taken in DMF to avoid the formation of the μ-oxo complex due to the attack of trace water on $Fe(TPP)(dmf)^+$ [15]. The solution infrared spectrum of 6.0 mM $[Fe(TPP)]_2(SO_4)$ in methylene chloride, following subtraction of the solvent spectrum, was consistent with the solid spectrum [2, 3].

Spectroscopy of $[Fe(P)]_2(SO_4)$ in the presence of added sulfate

When sulfate (as the PNP^+ salt) was added to solutions of $[Fe(TPP)]_2(SO_4)$ in chloroform, significant changes occurred in the visible, NMR and EPR spectra. The Soret band at 408 nm shifted to 417 nm, while the longer wavelength bands changed significantly with the appearance of bands at 577 and 630 (shoulder) nm, and the loss of bands at 508, 574, 652 and 681 nm (Fig. 1, Tables 1 and 2). These changes occurred at nearly stoichiometric concentrations of sulfate, and the spectrum was unchanged from a slight molar excess of sulfate to 10 mM, nearly the limit of solubility of the sulfate salt. Identical spectral changes were observed when sulfate was added to a solution of Fe(TPP)Cl. Reaction of $[Fe(TPP)]_2(SO_4)$ with one equivalent of sulfate in methylene chloride resulted in a product which had two strong sulfate infrared bands at 1135 and 1106 cm^{-1}, and a weaker band at 612 cm^{-1}.

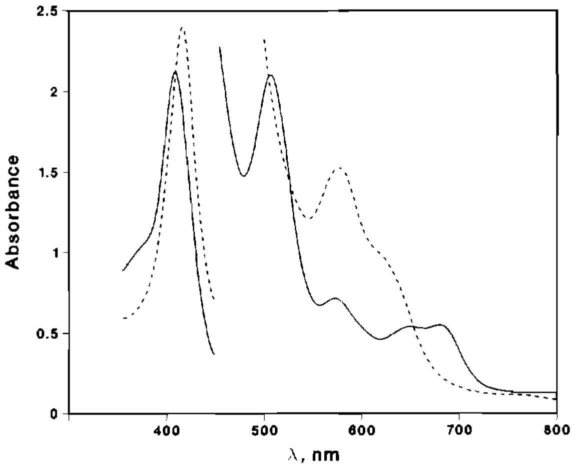

Fig. 1. Visible spectrum of $[Fe(TPP)]_2(SO_4)$ in chloroform in the presence and absence of sulfate. Solid line: 0 mM sulfate; dashed line: 2 mM sulfate. 360–475 nm in 1 mm cell; 476–800 nm in 1 cm cell.

As was previously reported [2], no EPR spectrum can be observed for $[Fe(TPP)]_2(SO_4)$. Upon the addition of sulfate, an EPR spectrum could be seen which was identical to other high-spin ferric complexes [2, 20]. Similarly, the proton NMR spectrum for $[Fe(TPP)]_2(SO_4)$ changed with the pyrrole resonance in $CDCl_3$ shifting from 71.6 to 77.7 ppm upon the addition of sulfate. The *o*- and *m*-phenyl resonances shifted from 12.7 to 13.4 ppm and from 11.2 to 12.0 ppm. The *p*-phenyl resonance shifted from 6.53 to 6.40 ppm. The magnetic susceptibility of the complex after addition of sulfate was 5.4 BM over the entire range of sulfate concentrations used, as determined by the Evans' method. This is consistent with a $S=5/2$ high-spin ferric complex, and is essentially unchanged from the sulfate-bridged dimer. In fact, after the addition of excess sulfate to the sulfate-bridged dimer, the proton NMR spec-

TABLE 2. Visible spectra of anionic ferric porphyrin complexes

Complex	Solvent	Soret[a] (nm)	Other visible bands[a] (nm)	Reference
$Fe(TPP)(SO_4)^-$	$CHCl_3$	417(240)	577(15), 630s	this work
	DMF	425(187)	567(15.8), 609(7.8), 660s	this work
	DMSO	426(272)	550s, 566(153), 619(80)	this work
$Fe(TPP)(4MeIm)_2^-$	DMA[b]	425	558, 598	16
$Fe(TPP)(CN)_2^-$	MeOH	424	539, 560, 596	17
$Fe(TPP)(OMe)_2^-$	DMSO	438	550, 597, 638	18
$Fe(TPP)(F)_2^-$	DMSO		531, 590, 631	19

[a] ϵ in parentheses, cm^{-1} mM^{-1}. [b] DMA = dimethylacetamide.

trum was virtually identical to that of Fe(TPP)Cl. Thus, while addition of sulfate to Fe(TPP)Cl caused significant changes in the visible spectrum, little or no changes were observed in the proton NMR spectrum under the same conditions.

Similar results were observed for $[Fe(OEP)]_2(SO_4)$ in chloroform (Tables 1 and 2). The Soret band at 386 nm shifted to 394 nm, and the long wavelength bands shifted from 500, 530, 580 (sh) and 628 nm to 473, 586 and 640 (sh) nm. The methylene resonance in the proton NMR for this complex shifted from 36.9 ppm in the absence of sulfate to 38.8 and 42.4 ppm with 1 equiv. of sulfate added (Table 3). These values are almost identical to Fe(OEP)Cl (39.0 and 42.4 ppm), another high-spin ferric complex. The methyl resonance shifted from 5.23 to 6.12 ppm at the same time (for Fe(OEP)Cl: 6.45 ppm).

The spectral changes of the sulfate-bridged dimer in DMF were difficult to follow due to the decomposition of the sulfate-bridged complex to the μ-oxo complex (Table 2). High concentrations of the complex minimized this decomposition, though. At high concentration of sulfate (10 mM), the Soret band shifted to 425 nm, and new bands at 567 and 609 nm appeared. Similar results were observed in DMSO with the Soret band at 426 nm, and the longer wavelength bands at 549(sh), 566 and 619 nm. The proton NMR spectra in DMF and DMSO showed significant changes upon the addition of sulfate. The minor pyrrole and phenyl bands observed with no added sulfate increased in height, while the major resonances decreased as more sulfate was added. When 2 mM sulfate was added to 0.5 mM sulfate-bridged porphyrin, the 68.1 ppm resonance in DMF disappeared and the 82.8 ppm resonance increased. Similar behavior was observed in DMSO except that, at these concentrations, the 74.1 ppm resonance could still be observed, though attenuated, and the 84 ppm resonance increased in height.

Electrochemistry of $[Fe(P)]_2(SO_4)$

Cyclic voltammetry of $[Fe(TPP)]_2(SO_4)$ in methylene chloride gave three waves [2], as shown in Fig. 2(A) and Table 4. The peak currents for the first two waves (waves Ia and Ib) were roughly equal in height and substantially less than the third wave. No anodic wave was observed for the second wave, and the shape of the first two waves was consistent with an irreversible process (either due to a slow electron transfer or a very fast irreversible following reaction). The ratio of the peak currents of the first two waves was independent of scan rate, and the peak currents increased with the square root of scan rate. The spectroelectrochemistry of the sulfate-bridged dimer was also examined using an OTTLE cell. The results are shown in Fig. 3. As the potential was scanned through the first two waves, the spectrum gradually changed to a mixture of a Fe(TPP) and

TABLE 3. Proton NMR spectra of ferric OEP complexes

Complex	Solvent	*meso*	Methyl	Methylene	Reference
$Fe(OEP)(SO_4)^-$	$CDCl_3$		6.12	38.8/42.4	this work
$Fe(OEP)(SO_3CF_3)$	$CDCl_3$	−24.6	7.2	34.6/49.4	21
$Fe(OEP)(ClO_4)$	$CDCl_3$	−5.5	6.38	35.5	22
$[Fe(OEP)]_2(SO_4)$	$CDCl_3$	−46.7	5.23	36.9	this work
	$CDCl_3$	−47.4	5.33	37.9	1, 2
$Fe(OEP)(HSO_4)$	$CDCl_3$			39.7/49.8	this work
Fe(OEP)(Cl)	$CDCl_3$		6.45	39.0/42.4	this work

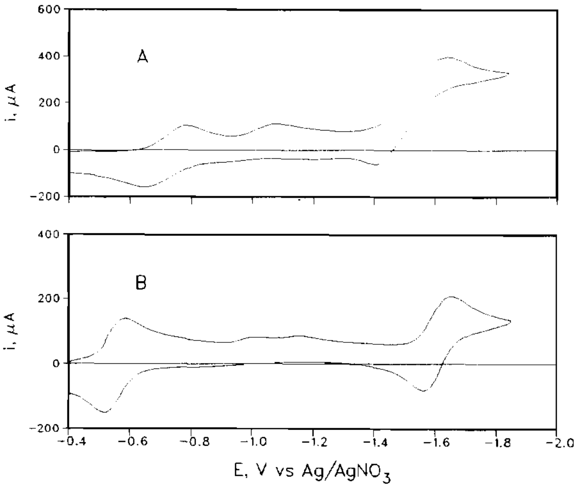

Fig. 2. Cyclic voltammetry of $[Fe(TPP)]_2SO_4$ in (A) methylene chloride and (B) DMSO. Supporting electrolyte was 0.1 M TBAP; working electrode is a platinum flag. Scan rate = 100 mV/s.

$Fe(TPP)(SO_4)^{2-}$ spectrum. The major Soret band was at 415 nm while a minor band at 441 nm was observed. In the long wavelength region, the 505, 569, 644 and 678 nm bands decreased while new bands appeared at 538, 570(sh) and 606 nm. Further reduction lead to the attenuation of the Soret band which was indicative of Fe(I)(TPP) [23, 24].

The NMR and EPR spectra of $[Fe(TPP)]_2SO_4$, reduced with borohydride, were also obtained. As borohydride was added to the sulfate-bridged dimer in $CDCl_3$, the 71.5 ppm pyrrole resonance decreased in height, and new pyrrole resonances at 77.6 and 4.6 ppm appeared. Similarly, reduction of the sulfate-bridged dimer lead to the appearance of a high-spin ferric EPR spectrum, from the initially EPR silent sulfate-bridged dimer.

Cyclic voltammetry of the sulfate-bridged dimer in DMSO was significantly different from the voltammetry in methylene chloride (Table 4). A typical voltammogram in DMSO is shown in Fig. 2(B). Only two major waves were observed, as is normally observed for ferric porphyrins. The ferric/ferrous wave for the sulfate-bridged dimer (−0.55 V) occurred at nearly the same potential as Fe(TPP)Cl (−0.53 V). The half-wave potential for the second wave was identical to that for Fe(TPP)Cl. In addition to the two major waves, two smaller waves (15 μA compared to 73 μA for the ferric/ferrous wave) were observed at −1.00 and −1.14 V in DMSO. Spectroelectrochemistry of the sulfate-bridged dimer in DMSO lead to spectra that were similar to Fe(TPP) and $Fe(TPP)^-$ [23–26].

Voltammetry of $[Fe(TPP)]_2(SO_4)$ in the presence of added sulfate

When sulfate (as the PNP^+ salt) was added to solutions of $[Fe(TPP)]_2(SO_4)$ in methylene chloride, the peak current for wave Ib increased while wave Ia decreased in height (Fig. 4). At sulfate concentrations greater than 2:1, the first reduction wave completely disappeared, and only two reduction waves were observed in the voltammetry. At this point, the ferric/ferrous wave was quite quasi-reversible, and the cathodic peak current and peak potential were independent of the concentration of sulfate. For example, at 50 mV/s, the ΔE_p value for

TABLE 4. Cyclic voltammetry of ferric porphyrin complexes in various solvents

Complex	Solvent	Wave Ia		Wave Ib		Wave II	
		E_{pc}[a]	i_{pc} (μA)	E_{pc}[a]	i_{pc} (μA)	$E_{1/2}$[a]	i_{pc} (μA)
$[Fe(TPP)]_2SO_4$	CH_2Cl_2	−0.76	125	−1.05	75	−1.50	360
$Fe(TPP)(ClO_4)$	CH_2Cl_2	−0.42	148			−1.50	170
Fe(TPP)Cl	CH_2Cl_2	−0.78	163			−1.48	190
$[Fe(OEP)]_2(SO_4)$	CH_2Cl_2	−1.03	93	−1.42	75		
Fe(OEP)Cl	CH_2Cl_2	−0.91	95			−1.72	108
$[Fe(TPP)]_2SO_4$	DMF	−0.58	83			−1.52	110
$Fe(TPP)(ClO_4)$[c]	DMF	−0.56	163			−1.47	165
Fe(TPP)Cl	DMF	−0.71	95			−1.51	170
$[Fe(OEP)]_2SO_4$	DMF	−0.68	100			−1.70	160
Fe(OEP)Cl	DMF	−0.94	95			−1.72	108
$[Fe(TPP)]_2SO_4$	DMSO	−0.55[b]	73	−1.00/−1.14	15/14	−1.61	115
Fe(TPP)Cl	DMSO	−0.53[b]	65			−1.59	60
$[Fe(OEP)]_2(SO_4)$	DMSO	−0.69[b]	80	−1.2/−1.32	< 1/2	−1.78	88
Fe(OEP)Cl	DMSO	−0.69[b]	68			−1.79	53

[a] V vs. $Ag/AgNO_3$; [Fe(P)X] = 0.5 mM. [b] $E_{1/2}$. [c] [Fe(P)X] = 1.0 mM.

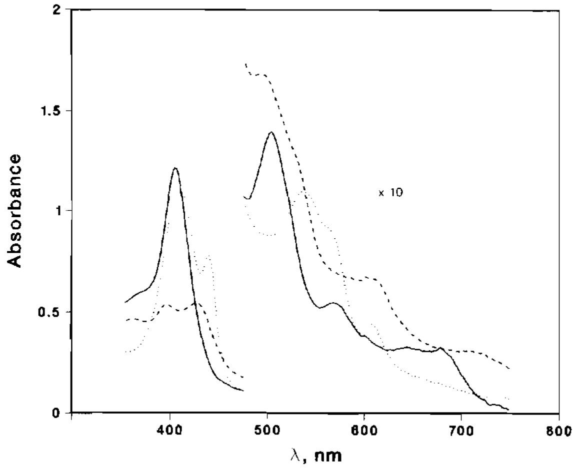

Fig. 3. Spectroelectrochemistry of 0.2 mM $[Fe(TPP)]_2(SO_4)$ in methylene chloride in OTTLE cell. Solid line: 0 V vs. SRE; dotted line: −0.9 V vs. SRE; dashed line: −1.8 V vs. SRE. 476–750 nm region was multiplied by a factor of 10.

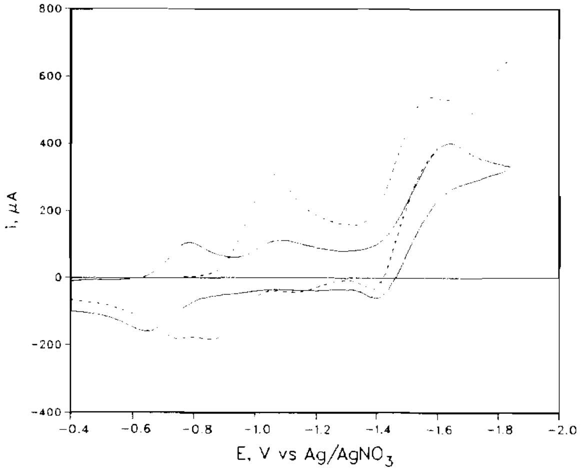

Fig. 4. Cyclic voltammetry of $[Fe(TPP)]_2(SO_4)$ in the presence and absence of sulfate in methylene chloride. Solid line: 0 mM sulfate; dotted line: 1 mM sulfate; dashed line: 10 mM sulfate. Concentration of $[Fe(TPP)]_2(SO_4)$: 0.5 mM; platinum working electrode; scan rate = 100 mV/s.

the ferric/ferrous wave was 350 mV. At higher concentrations of sulfate (10 mM), wave Ib became much more reversible, especially at slow scan rates (ΔE_p at 50 mV/s = 115 mV). This increased reversibility is due to the growth of a new anodic peak at about −0.9 V, and the disappearance of the anodic peak at −0.7 V. At 10 mM sulfate, the $E_{1/2}$ of the ferric/ferrous wave was −0.97 V versus $Ag/AgNO_3$. The spectroelectrochemistry of the sulfate dimer in methylene chloride in the presence of added sulfate showed some distinct differences from its behavior in the absence of added sulfate. The visible spectrum of the ferrous species had Soret bands at 418 and 440 nm, and long wavelength bands at 504, 537, 569 and 609 nm (Fig. 5). Further reduction gave rise to an iron(I) spectrum.

Cyclic voltammetry of the sulfate-bridged dimer in DMSO was qualitatively similar to the results in methylene chloride (Table 4). Higher concentrations of sulfate were needed to cause the appearance of the new first wave at about −1.0 V. As the concentration of sulfate increased, the minor wave at −1.00 V increased in height, and the major first wave at −0.55 V decreased. Above 1.0 mM, the original first wave at −0.55 V was not seen. In addition to the wave at −1.00 V, a small wave also was observed at −1.14 V. For low concentrations of sulfate, this wave was about equal in height to the −1.00 V wave, but it decreased in height as the concentration of sulfate increased. It was not observed above 5 mM sulfate. The Fe(II)/Fe(I) wave was unaffected by the concentration of sulfate and occurred at −1.60 V. The spectroelectrochemistry of the sulfate-bridged dimer in DMSO was similar whether in the presence or absence of sulfate.

Because water is known to be an impurity in DMSO, as well as the fact that trace water may be present in the sulfate salts, the effect of water on the voltammetric behavior of the sulfate-bridged dimer in DMSO was examined. As shown above, two waves are observed in DMSO where one wave was observed in methylene chloride (wave Ib). The more negative wave (−1.18 V) decreased as the concentration of sulfate increased. As a result, with 10 mM sulfate, the sulfate-bridged dimer has two major waves at −1.07 V (E_{pc}, ferric/ferrous reduction, wave Ib) and −1.62 V ($E_{1/2}$, iron(II)/iron(I) reduc-

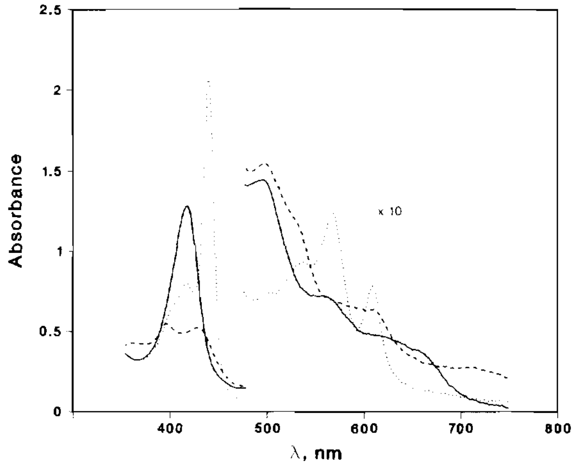

Fig. 5. Spectroelectrochemistry of 0.2 mM $[Fe(TPP)]_2(SO_4)$ in methylene chloride in the presence of 5 mM sulfate in an OTTLE cell. Solid line: −0.4 V vs. SRE; dotted line: −1.0 V vs. SRE; dashed line: −1.8 V vs. SRE. 476–750 nm region was multiplied by a factor of 10.

tion, wave II). A smaller wave at about −1.18 V (wave Ic) was also seen (less than 2 μA compared to 68 μA for the ferric/ferrous wave). Wave Ic was more significant at lower concentrations of sulfate, and was about equal in height to wave Ib with no added sulfate. As the concentration of water increased above 1 mM (concentration of sulfate was 10 mM), the height of wave Ib decreased while wave Ic increased in height. At 111 mM water, waves Ib and Ic were about equal in height. The peak potentials were relatively unchanged with the addition of water, but they were difficult to measure accurately because they were not well separated. The sum of the peak currents for waves Ib and Ic was nearly equal to the current due to wave II. The total currents decreased about 25% due to the increased viscosity of the DMSO/water mixed solvent and to the dilution of the solution.

Spectroscopy and voltammetry of $Fe(P)(HSO_4)$

The hydrogen sulfate complex of Fe(OEP) was obtained by using high concentrations of sulfuric acid in the decomposition of the μ-oxo complex. Alternatively, this complex could be generated *in situ* by addition of $(TBA)(HSO_4)$ to $Fe(P)(ClO_4)$. The TPP complex appeared to be much less stable than the OEP complex, though, the stability was not extensively studied in this work. The hydrogen sulfate complex appeared to decompose to the sulfate dimer and, presumably, sulfuric acid [5]. The visible spectroscopy of $Fe(OEP)(HSO_4)$ is summarized in Table 1. The Soret band was at 382 nm, and the long wavelength bands were observed at 504 and 636 nm. The infrared spectrum of $Fe(OEP)(HSO_4)$ gave rise to new bands at 917, 886 and 584 cm^{-1}. In this region, the sulfate dimer had bands at 915, 896, 667, 619 and 579 cm^{-1}. These results were quite similar to $Fe(TPP)(HSO_4)$ [3]. The proton NMR spectrum (Table 3) in $CDCl_3$ was also different from the sulfate dimer, with resonances at 49.8 and 39.7 ppm. These compare to values of 36.9 ppm for the sulfate dimer, and 42.4 and 39.0 ppm for Fe(OEP)(Cl).

In the absence of bisulfate, $Fe(TPP)(ClO_4)$ was reduced with a half-wave potential of −0.378 V versus SRE. With the addition of 1 equiv. of HSO_4^- (as the TBA^+ salt), the wave shifted to −0.392 V versus SRE. No new waves were observed between the iron(III) and iron(II) reduction waves. Further additions of bisulfate caused the wave to shift to more negative potentials (−0.428 V at 1.5 mM; −0.442 V at 2.9 mM; and −0.472 V at 10.8 mM bisulfate). With time, a new wave appeared at about −0.85 V, and eventually grew with time until it equaled the height of the first wave. Visible spectroscopy of the solution at this point yielded a spectrum that was identical to the Fe(TPP) sulfate dimer. The addition of up to 5.0 mM bisulfate had no effect on either wave of $Fe(TPP)(ClO_4)$ in DMF, with the iron(III) wave occurring at −0.53 V versus SRE in the presence and absence of bisulfate.

Discussion

Effect of solvent on the structure of $[Fe(TPP)]_2SO_4$

As was consistent with earlier work [1, 2], the sulfate-bridged dimer was stable in non-coordinating solvents such as chloroform and methylene chloride. This was confirmed by proton NMR and infrared spectroscopy, as evidenced by the similarity of the solid and solution infrared spectra. In coordinating solvents such as DMF and DMSO, the dimer dissociated to form the solvent coordinated complex, $Fe(TPP)(S)_2^+$, where S = DMSO or DMF. Small amounts of the sulfate complex could be observed in the NMR and visible spectrum. As confirmation of this assignment, the NMR spectrum of the sulfate-bridged dimer was similar to the known spectra of DMF and DMSO coordinated ferric TPP [27]. Thus, the following equilibria occur in these solvents

$$[Fe(TPP)]_2SO_4 + 2S \rightleftharpoons Fe(TPP)(S)_2^+ + Fe(TPP)(SO_4)^- \quad (1)$$

$$Fe(TPP)(SO_4)^- + 2S \rightleftharpoons Fe(TPP)(S)_2^+ + SO_4^{2-} \quad (2)$$

In DMF and DMSO, reaction (1) goes to completion, while reaction (2) favors the right side. In DMSO, where Fe(TPP)Cl forms $Fe(TPP)(dmso)_2^+$, the half-wave potentials of Fe(TPP)Cl and the sulfate-bridged dimer are nearly identical.

Electrochemical behavior of the sulfate-bridged dimer

In methylene chloride, the dimer is stable in solution, and two waves are observed for the ferric/ferrous reduction. Wave Ia is due to the reduction of the dimer itself.

$$[Fe(TPP)]_2SO_4 + e^- \longrightarrow Fe(TPP) + Fe(TPP)(SO_4)^- \quad (3)$$

Because the ferric sulfate adduct is relatively strong in methylene chloride, additional reduction of the sulfate complex is more difficult due to the coulombic repulsion of the negatively charged porphyrin complex. The sulfate complex can be observed, though, in the NMR (δ = 77.6 ppm) and EPR spectra, and Fe(TPP) (δ = 4.6 ppm) can be seen in the NMR spectrum of the partially reduced porphyrin dimer. Wave Ib is due to the reduction of the sulfate adduct.

$$Fe(TPP)(SO_4)^- + e^- \longrightarrow Fe(TPP) + SO_4^{2-} \qquad (4)$$

Spectroelectrochemical reduction of the sulfate-bridged dimer yielded mostly the uncoordinated Fe(TPP) complex, though some sulfate remained coordinated to the ferrous porphyrin, as evidenced by the weak 440 nm Soret band.

$$Fe(TPP) + SO_4^{2-} \rightleftharpoons Fe(TPP)(SO_4)^{2-} \qquad (5)$$

In DMSO, sulfate coordinated relatively weakly, or not at all, with the ferric porphyrin complex, and the reduction involved mainly the reduction of the solvent coordinated ferric complex. In any case, spectroelectrochemistry of the sulfate-bridged dimer gave rise to solvent coordinated ferrous porphyrin complexes.

Spectroscopy and reduction of [Fe(TPP)]$_2$SO$_4$ in the presence of sulfate

For all the solvents studied, the addition of sulfate to a solution of the sulfate-bridged dimer gave rise to the ferric sulfate complex. In chloroform and methylene chloride, this lead to the dissociation of the complex into monomeric species

$$[Fe(TPP)]_2SO_4 + SO_4^{2-} \longrightarrow 2Fe(TPP)(SO_4)^- \qquad (6)$$

or, in DMF and DMSO, displacement of solvent

$$Fe(TPP)(S)_2^+ + SO_4^{2-} \longrightarrow Fe(TPP)(SO_4)^- + 2S \qquad (7)$$

The visible spectrum of the sulfate complex was quite different from other five-coordinated ferric porphyrin species. The spectral changes were similar to what was observed for anionic ferric porphyrin complexes, which are generally six coordinate. The results are summarized in Table 2. In particular, the Soret band shifted to longer wavelengths, and the 680–700 nm band disappeared. This was seen for both low-spin (imidazole and cyanide) and high-spin (fluoride and methoxide) complexes. The bands between 500–650 nm do not appear to correlate well with spin state or coordination number. The infrared spectrum of $[Fe(TPP)]_2(SO_4)$ in methylene chloride with added sulfate was similar to that of a monomeric ferric porphyrin sulfate complex [28]. The splitting of the free sulfate band at 1104 cm^{-1} was consistent with this assignment. The magnetic susceptibility and proton NMR spectrum were consistent with a high spin ($S = 5/2$) complex.

In methylene chloride, sulfate forms a relatively strong complex or ion pair. The half-wave potential for Fe(TPP)Cl in methylene chloride was -0.64 V, which shifted to -0.97 V for the sulfate complex. This shift of 320 mV indicates that sulfate formed a complex that is about 2.7×10^5 times stronger than chloride. Such strong complexes were not observed in DMF or DMSO, where the dimer itself was essentially dissociated into the solvent coordinated complexes without excess sulfate. The strong sulfate complex in methylene chloride is probably due to ion pairing in this solvent, because sulfate (dianionic) is poorly solvated in this solvent. In more coordinating solvents, ion pairing effects are minimized and the strength of the iron sulfate complex is relatively weaker. The spectroelectrochemistry of the sulfate complex in methylene chloride with added sulfate, which gave a visible spectrum characteristic of $Fe^{II}(P)(X)^-$ complexes [26], indicated that the sulfate remained coordinated upon reduction if sufficient sulfate was present. Therefore, under these conditions, the sulfate remained coordinated.

$$Fe(TPP)(SO_4)^- + e^- \longrightarrow Fe(TPP)(SO_4)^{2-} \qquad (8)$$

The appearance of the ferrous sulfate complex correlates well with the growth of the new anodic peak at -0.9 V, and the increased reversibility of wave Ib. The quasi-reversibility of this wave in all the solvents is no doubt due to the slow rate of sulfate coordination. The EC mechanism for the ferric reduction has been shown to occur for Fe(TPP)Cl by Lexa *et al.* [15].

The voltammetric and spectroscopic behavior of the sulfate-bridged dimer in DMSO indicated that sulfate will coordinate with iron at high enough concentrations of sulfate (reaction (7)). The spectroscopic properties of the sulfate complex were quite similar to the spectrum in methylene chloride, but significantly different from other high-spin ferric porphyrin complexes. The appearance of wave Ic is probably related to trace water that is in the solvent. Water apparently stabilizes the ferric oxidation state, either by solvating the sulfate part of the complex or by complexing with the iron. Further addition of sulfate probably shifts the equilibrium of the trace water in the solvent so that the free sulfate (a dianion which is poorly solvated in DMSO) is preferentially solvated rather than the porphyrin anion. Addition of extra water shifted this equilibrium back so that wave Ic reappeared.

Ferric porphyrin bisulfate complexes

A single NMR spectrum was obtained for $Fe(OEP)(HSO_4)$ in methylene chloride, indicating that there was only one ferric species present at equilibrium. The visible spectrum was quite similar to $Fe(OEP)(ClO_4)$. While a previous report showed that $Fe(TPP)(HSO_4)$ was unstable in solution [5], the ferric OEP complex appears to be more stable, with no changes in the visible spectrum over a period of 30 min.

The cyclic voltammetry of Fe(TPP)(HSO_4), generated by the addition of HSO_4^- to Fe(TPP)(ClO_4), indicated that the bisulfate complex was quite weak, and not much stronger than the perchlorate complex. From the shift in half-wave potentials, a formation constant of 5 in methylene chloride can be calculated for the displacement of perchlorate. In DMF, where the ferric porphyrin is coordinated with DMF rather than the anion ligand, no displacement of DMF was observed, as evidenced by the fact that the half-wave potential of th ferric porphyrin reduction was independent of bisulfate concentration.

Conclusions

The sulfate-bridged dimer appears to be stable only in non-coordinating solvents such as methylene chloride or chloroform. In DMF and DMSO, the dimer is essentially dissociated, and the voltammetry is due to the reduction of Fe(P)(SO_4)$^-$ or Fe(P)(S)$^+$, where S is the solvent. Addition of sulfate to solutions where the sulfate dimer is stable, leads to dissociation of the dimer into sulfate complexes. The reaction is almost stoichiometric in chloroform. While the proton NMR and magnetic susceptibility measurements indicate a high-spin ferric porphyrin species for the sulfate complex, the visible spectrum is significantly different from the five-coordinate complexes. From the spectroelectrochemistry and voltammetry in methylene chloride, the ferrous sulfate complex can be formed, similar to the other anions. Bisulfate formed extremely weak complexes with ferric porphyrins, and could only be observed in low dielectric solvents such as methylene chloride.

Acknowledgements

We would like to acknowledge the University of Wisconsin, Milwaukee, for the use of the 250 MHz Bruker NMR. We would also like to acknowledge William Antholine and Jana Narasimhan of the Medical College of Wisconsin for obtaining the EPR spectra.

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