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Reaction of low-valent iron porphyrins with alkyl containing supporting electrolytes

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Abstract

A σ-alkyl iron porphyrin complex was found to be formed from the reaction of $Fe(TPP)^{2-}$ with tetraalkylammonium ions (TPP = tetraphenylporphyrin). At room temperature, this reaction was too slow to be observed with cyclic voltammetry. But, if one electrolyzes at a potential that generated $Fe(TPP)^{2-}$, and then initiates the scan in the forward direction, waves for $Fe(TPP)(R)^{-}/Fe(TPP)(R)$ and $Fe(TPP)(R)/Fe(TPP)(R)^{+}$, where R = alkyl group, were observed. Both tetramethyl- and tetrabutylammonium ions were found to react with $Fe(TPP)^{2-}$. No alkylated products were observed if alkali salts were used as the supporting electrolyte. Visible spectroelectrochemistry with a thin layer cell showed that electrolysis at the first and second waves of Fe(TPP)(Cl) in DMF yielded the expected Fe(TPP) and $Fe(TPP)^{-}$ complexes, but $Fe(TPP)^{2-}$ was not observed at the third wave. Instead, the spectrum of $Fe(TPP)(R)^{-}$ was obtained. Oxidation of this species led to the formation of Fe(TPP)(R), and further oxidation regenerated Fe(TPP)(Cl) because of the poor stability of $Fe(TPP)(R)^{+}$. Further characterization was carried out by obtaining the resonance Raman spectra of chemically generated $Fe(TPP)(CH_3)^{0/-}$ and $Fe(TPP)(butyl)^{0/-}$ complexes, and comparing the results with the electrochemically generated complexes. The σ-alkyl iron porphyrins were not very stable under laser irradiation, and the best spectra were obtained in THF with frozen samples. The σ-alkyl ferric porphyrins were considerably less stable than the corresponding ferrous complexes, and the photoproduct, Fe(TPP), could be observed in all spectra. The ferrous alkyl porphyrins gave spectra that were consistent with low-spin five-coordinate complexes, with ν_2 and ν_4 bands being observed at 1566 and 1363 cm^{-1}, respectively. The ν_2 and ν_4 bands for the ferric alkyl porphyrin were at 1565 and 1359 cm^{-1}, respectively. The product, obtained by electrolyzing Fe(TPP)(Cl) at the potential for the generation of $Fe(TPP)^{2-}$, gave a spectrum in THF that was consistent with an iron alkyl complex. The photoproduct appeared to be $Fe(TPP)(OH)^{-}$ rather than Fe(TPP), as was observed in the chemically generated product due to trace amounts of water in the supporting electrolyte. The visible spectrum of the resonance Raman was identical to the authentic $Fe(TPP)(R)^{-}$ sample. There was no evidence for $Fe(TPP)(OH)^{-}$, which would have been quite apparent in the visible spectrum. The generation of $Fe(TPP)(R)^{-}$ from $Fe(TPP)^{2-}$ and tetrabutylammonium ion could occur by at least two pathways: nucleophilic attack or electron transfer between iron('0') on the tetrabutylammonium ion. Steric effects would favor an electron transfer mechanism over the nucleophilic process, but the data at this time are not conclusive.

Keywords: Electrochemistry; Iron complexes; Porphyrin complexes; Low-valent complexes

1. Introduction

Electrochemical methods have been quite valuable as an efficient method for the generation of materials that have very low (very high) redox potentials without the use of reducing (oxidizing) agents. Unfortunately, efficient generation of these complexes normally requires the use of supporting electrolytes in significant amounts, which can affect the stability of the redox product. Some of the most common supporting electrolytes are the tetraalkylammonium salts, which are used because of their solubility, wide potential window and inertness. But, there have been several reports in the literature where the electrogenerated product can react with this cation. For example, Saveant and Su [1] have postulated that a quaternary butyl triphenylphosphine radical, which was formed when the electrogenerated triphenylphosphine radical anion was alkylated by the tetrabutylammonium (TBA^{+}) cation, was an intermediate in a catalytic process. Decomposition of this quaternary phosphonium ion regenerated triphenylphosphine and a butyl radical, and the phosphine could be further reduced. The electrogenerated succinimide radical anion was found to react with TBA^{+} at elevated temperatures to form *N*-n-butylsuccinimide [2]. Niyazymbetov et al. [3] observed that

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electrogenerated thiols nucleophilically attacked tetraalkylammonium ions to form thioethers and trialkylamines.

Direct reduction of the tetrabutylammonium ion at a gold electrode was found to lead to the reductive cleavage of the C–N bond to form tributylamine and butyl radical [4]. An alternate pathway for tetraalkylammonium reduction was the cathodic corrosion of the electrode [5]. In this case, metal–tetraalkylammonium complexes are formed, and the cation remains intact [5]. These processes occur at potentials negative of the iron(I) porphyrin reduction wave, and no cathodic corrosion has been observed at platinum [6].

Iron('0') porphyrins have been generated in solvents such as THF using chemical reducing agents, and were found to be quite stable. Visible spectra [7], X-ray structures [8], ^{2}H NMR [9] and resonance Raman [10] spectra have all been reported. Typical reducing agents were sodium naphthalide (anthracenide) or a sodium mirror. Stable iron('0') porphyrin complexes could not be obtained in our work using electrochemical methods, and studies were initiated to understand the chemistry of this process. Low-valent iron porphyrins (iron(I) or iron('0')) have been shown to react with a wide variety of organic compounds by either a nucleophilic or electron transfer process to yield σ-bonded complexes. The reaction of iron(I) or iron('0') with alkyl halides can lead to σ-alkyl iron porphyrins by a dissociative electron transfer or S_N2 substitution [11–13]. A similar behavior was observed for the reaction of Fe('0')$^{2-}$ with acetic anhydride to yield Fe(II)–COR, a σ-acyl porphyrin, and RCO_2^- [14]. Under the same conditions, Fe(I) reacted several orders of magnitude slower than Fe('0'), but also led to a σ-acyl porphyrin. The chemical reduction of iron(III) prophyrins by sodium borohydride has been shown to lead to the reduction of alkenes and alkynes via σ-alkyl iron porphyrin intermediates [15]. Finally, iron('0') porphyrins have been shown to catalyze the electrochemical reduction of carbon dioxide [16,17]. Our studies also indicated that a σ-alkyl complex was being generated instead of iron('0'), and the most likely source of the alkyl group was the tetraalkylammonium supporting electrolyte. In order to verify this mechanism, the following study was undertaken.

2. Experimental

2.1. Chemicals

Chlorine-free iron(III) tetraphenylporphyrin chloride was purchased from MidCentury Chemicals, and was used as received. Tetrahydrofuran (THF) (Aldrich Chemical Co.) was doubly distilled from potassium by heating at reflux temperatures under a dinitrogen atmosphere until the blue benzophenone anion radical was persistent. Dimethylformamide (DMF) (Aldrich Chemical Co.) was purified by heating at reflux temperatures over calcium hydride, followed by distillation under reduced pressure. Care has been taken to avoid exposure to the atmosphere by flushing the receiving containers with argon gas. Dimethyl sulfoxide (DMSO), anhydrous grade (Aldrich Chemical Co.) was used as received. All solvents were stored in an argon atmosphere.

Tetrabutylammonium perchlorate (TBAP) was obtained from GFS Chemical Co. It was dried under vacuum at 70 °C for several hours, and stored under an argon atmosphere, except when noted in the text. In that case, it was recrystallized twice from absolute ethanol, and dried at 75 °C under a vacuum for 12 h. Sodium perchlorate, lithium perchlorate and sodium nitrate were obtained from Aldrich Chemical Co. Tetramethylammonium perchlorate (TMAP) was purchased from Sigma Chemical Co. The other salts were used as received. The σ-methyl- and butyl-ferrous and -ferric–TPP complexes were synthesized by literature procedures [18] using the appropriate Grignard reagent.

2.2. Instrumentation

The cyclic voltammetric data were obtained with a Cypress System CYSY-1R potentiostat (Version 6.0 software). A three-electrode cell was used for voltammetric measurements, consisting of a platinum wire or flag working electrode, a platinum flag auxiliary electrode, and an Ag/0.1 M $AgNO_3$ in acetonitrile reference electrode. The reference electrode was separated from the electrochemical test solution by a salt bridge filled with the appropriate solvent and supporting electrolyte. An optically transparent thin layer electrochemical (OTTLE) cell was used for the spectroelectrochemical experiments [19]. The UV–Vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Controlled potential electrolysis was performed with an Electrosynthesis Co. model 410 potentiostatic controller with an EG&G PARC model 379 digital coulometer. Resonance Raman spectra were obtained with a Kr^+ laser (Spectraphysics model 1100) using 413 nm excitation, with a 1269 SPEX single monochromator equipped with a charge coupled detector (CCD). When appropriate, samples were frozen by passing nitrogen gas cooled at liquid nitrogen temperatures over the sample.

3. Results and discussion

3.1. Cyclic voltammetry

The electrochemical reduction of Fe(TPP)(Cl) occurs in three one-electron waves as shown below.

$$\mathrm{Fe^{III}(TPP)(Cl)} + e^- \rightleftharpoons \mathrm{Fe^{II}(TPP)} + \mathrm{Cl^-} \qquad \text{Wave 1}$$

$$\mathrm{Fe^{II}(TPP)} + e^- \rightleftharpoons \mathrm{Fe^{I}(TPP)^-} \qquad \text{Wave 2}$$

$$\mathrm{Fe^{I}(TPP)} + e^- \rightleftharpoons \mathrm{Fe(TPP)^{2-}} \qquad \text{Wave 3}$$

A typical voltammogram in DMF is shown in Fig. 1(A), where the primed numbers are used to indicate the oxidation waves. All the waves appear to be quasi-reversible to reversible on the voltammetric time scale. In order to observe slow reactions of $\mathrm{Fe(TPP)^{2-}}$, the electrode potential was poised in the diffusion controlled region of the third wave for a period of time, and then the scan was initiated in the positive direction. Two new oxidation (and reduction) waves were observed (Fig. 1(B)) at −1.22 (wave 4′) and −0.058 (wave 5′) V versus $\mathrm{Ag/AgNO_3}$. These new waves corresponded to the potentials observed by other workers [12,14,20] for the $\mathrm{Fe(III)(P)(R)/Fe(II)(P)(R)^-}$ and the $\mathrm{Fe(IV)(P)(R)^+/Fe(III)(P)(R)}$ waves, respectively. The results are summarized in Table 1. If the temperature of the solution was reduced to below 0 °C, these new waves, attributed to the σ-alkyl iron porphyrins, were not observed (Fig. 1(C)), nor were these waves observed when alkali salts were used. Electrolysis at the iron(I) potential, followed by a positive scan showed no evidence of iron–alkyl complex formation. The reduction mechanism in the presence of TBAP can be summarized as follows.

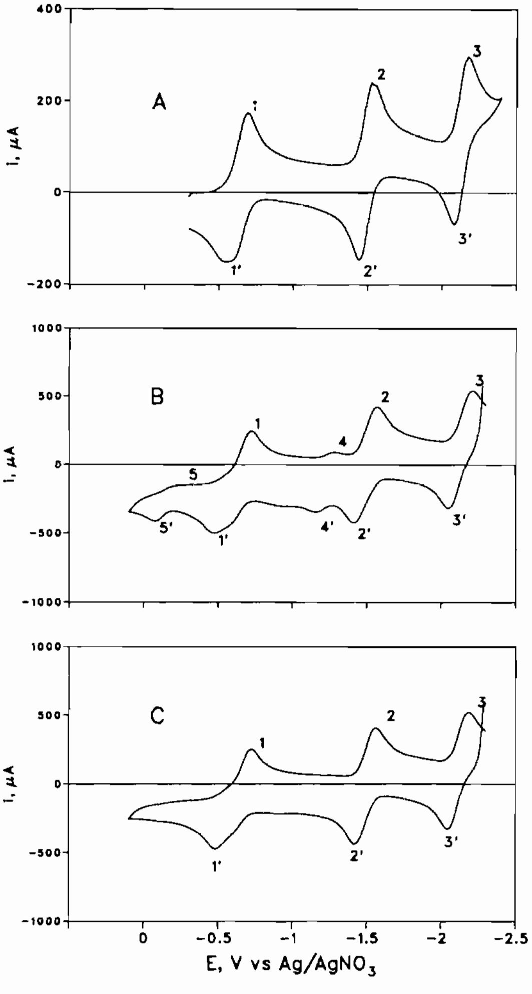

Fig. 1. Cyclic voltammetry of Fe(TPP)(Cl) in DMF. (A) Scan initiated at −0.3 V; scan rate = 50 mV s^{-1}. (B) Potential poised at −2.2 V for 3 min, then scan initiated towards a positive potential; scan rate = 300 mV s^{-1}; temperature = 22 °C. (C) Potential poised at −2.2 V for 3 min, then scan initiated towards a positive potential; scan rate = 300 mV s^{-1}; temperature = −5 °C. Working electrode = platinum; supporting electrolyte = 0.10 M TBAP.

$$\mathrm{Fe^{I}(TPP)} + e^- \rightleftharpoons \mathrm{Fe(TPP)^{2-}} \qquad \text{Wave 3}$$

$$\mathrm{Fe(TPP)^{2-}} + \mathrm{R_4N^+} \longrightarrow \mathrm{Fe^{II}(TPP)(R)^-} + \mathrm{R_3N}$$

$$\mathrm{Fe^{II}(TPP)(R)^-} \longrightarrow \mathrm{Fe^{III}(TPP)(R)} + e^- \qquad \text{Wave 4}'$$

$$\mathrm{Fe^{III}(TPP)(R)} \longrightarrow \mathrm{Fe^{IV}(TPP)(R)^+} + e^- \qquad \text{Wave 5}'$$

Waves 4′ and 5′, and their corresponding reduction waves (waves 4 and 5) were observed in DMSO and THF, in addition to DMF. Additional purification of the supporting electrolyte, as noted in Section 2, had no effect on the voltammetric behavior.

3.2. *Visible spectroscopy*

In order to characterize the reduction products, thin layer visible spectroelectrochemistry (OTTLE) was performed. Electrolysis at the first and second wave yielded the spectra for $\mathrm{Fe^{II}(TPP)}$ and $\mathrm{Fe^{I}(TPP)^-}$ (Fig. 2(A)), respectively, as expected (Table 2). If the potential of the working electrode was maintained at the potential for the generation of $\mathrm{Fe(`0')(TPP)^{2-}}$, the visible spectrum of Fe(‘0’) porphyrin was not obtained in the presence of tetraalkylammonium salts, but rather a spectrum that corresponded to $\mathrm{Fe^{II}(TPP)(R)^-}$ (Fig. 2(A), Table 2). It should be noted that the Soret bands for iron(‘0’) porphyrins are extremely weak, and may be difficult to observe in the presence of iron(II) species, though there should be evidence for iron(‘0’) in the 500–800 nm region. The oxidation of this species at a potential positive of wave 4′ generated the $\mathrm{Fe^{III}(TPP)(R)}$ spectrum, with no evidence for the $\mathrm{Fe^{II}(TPP)}$ complex. Further oxidation regenerated Fe(TPP)(Cl), due to the instability of $\mathrm{Fe^{IV}(TPP)(R)^+}$. If alkali ions such as sodium or lithium are substituted for tetrabutylammonium ion, the σ-alkyl iron porphyrin spectrum was not observed, but a spectrum, reported earlier by Kadish et al. [22] was obtained. This spectrum has been attributed to $\mathrm{Fe(TPP)(OH)^{2-}}$ (Fig. 2(A), Table 2). Oxidation of the $\mathrm{Fe(TPP)(OH)^{2-}}$ complex led to the formation of the μ-oxo complex, $\mathrm{Fe(TPP)_2O}$. These results indicate that the electrolyte system contained trace amounts of water which may be due to the hygroscopic nature of the alkali metal perchlorates.

Table 1
Cyclic voltammetry of Fe(TPP)(Cl) in various solvents and supporting electrolytes

Solvent	Electrolyte	$E_{1/2}$ (V)					Ref.
		Fe(III)/Fe(II)	Fe(II)/Fe(I)	Fe(I)/Fe('0')	Fe(III)R/Fe(II)R	Fe(IV)R/Fc(III)R	
DMF	TBAP	−0.62	−1.50	−2.12	−1.23	0.080	this work
	TBAP/n-BuBr		−1.43^{a}	−2.05^{a}	−1.17^{a,b}		[12]
	TEAP/acetic anhydride				−1.02^{a,c}	−0.05^{a,c}	[14]
DMF	TMAP	−0.65	−1.49	−2.16	−1.23	−0.092	this work
DMF	$NaClO_4$	−0.62	−1.50	−2.21			this work
DMF^{a}	$LiClO_4$	−0.61	−1.54	−2.16			this work
DMSO	TBAP	−0.55	−1.62	−2.14	−1.22	−0.082	this work
DMSO	TMAP	−0.53	−1.59	−2.06	−1.22	−0.088	this work
DMSO	$NaClO_4$	−0.55	−1.60	−2.12^{d}			this work
THF	TBAP	−0.76	−1.58	−2.13	−1.29	^{e}	this work
CH_2Cl_2	TBAP	−0.69	−1.48		−1.27	^{e}	this work

[a] Potentials corrected for reference electrode: $E(Ag/AgNO_3) = E(SCE) - 0.45$ V.
[b] Fe(C_{12}TPP) porphyrin.
[c] R = CH_3–CO–.
[d] Irreversible wave.
[e] Region not scanned.

Table 2
Visible spectra of iron porphyrins

Compound	Solvent	Soret^{a}	Other bands^{a}	Ref.
Fe(TPP)$^{-}$	THF	390, 423	510, 575, 605s, 674	this work
	DMF	395, 425	506, 577, 665, 712	this work
	DMSO	396, 428	515, 604, 668, 712	this work
Fe(TPP)(butyl)$^{-}$	THF	364, 430	502, 532, 608, 720	this work
Fe(C_{12}TPP)(butyl)$^{-}$	DMF	306(36), 364(49.5), 423(84.2)	502(93.6), 530(77.2), 609(33.4), 714(14.7)	[13]
Fe(TPP)(butyl)	THF	400s, 424	524	this work
	benzene	392(75), 412(138)	518(10.8), 552(5.6)	[21]
Fe(C_{12}TPP)(butyl)	DMF	397s, 416(134)	522(72.6), 538s	[13]
Fe(TPP)(methyl)$^{-}$	THF	362, 426	502, 532, 604, 714	this work
Fe(TPP)(methyl)	THF	400s, 424	528	this work
	benzene	390(66), 413(144), 425s	518(12.0), 546(7.3)	[21]
Fe(TPP)(OH)$^{2-}$	DMF	360, 460	526, 556	this work
	DMF	362, 457	525, 555s	[22]
Fe(TPP)(butyl)$^{-\,b}$	THF	362, 436	502, 532, 605, 712	this work
	DMF	362, 430	500, 532, 602, 712	this work
	DMSO	362, 392, 434s, 449	524, 608, 716	this work

[a] Wavelength in nm (molar absorptivities, mM^{-1} cm^{-1}).
[b] Electrochemically generated.

3.3. Resonance Raman spectroscopy

Iron(III) and iron(II) alkyl porphyrins can be independently synthesized [21,23], and they have considerable stability in THF if protected from dioxygen and light [23]. Resonance Raman spectra of Fe(TPP)(CH_3) in benzene and carbon disulfide have been reported [24]. Both oxidation states of iron are quite photolabile, and it was difficult to obtain spectra completely free of photoreduced product. Li and Goff [18] have previously shown that Fe^{III}(TPP)(CH_3) will homolytically cleave to form Fe^{II}(TPP) and methyl radical. Typical spectra of alkyl ferric and ferrous porphyrins are shown in Fig. 3(A) and (B), and are summarized in Table 3. The greatest stability was obtained for frozen solutions, and low laser powers. The iron(II) alkyl complex was considerably more stabile towards photodecomposition than the iron(III) alkyl. The main structural features of Fe^{II}(TPP)(butyl)$^{-}$ are the ν_2 bands at 1540 and 1566 cm^{-1} and the ν_4 bands at 1343 and 1363 cm^{-1}. The lower frequency bands at 1343 and 1540 cm^{-1} were consistent with the photodecomposition product, Fe(TPP) in THF [27]. The higher frequency bands are similar to the bands observed for the low-spin five-coordinate complexes, such as Fe(TPP)(NO) (see Table 3). High-spin ferrous complexes in THF display ν_2 bands around 1540–1546 cm^{-1}. The ν_4 band at 1363 cm^{-1} is once again similar to the

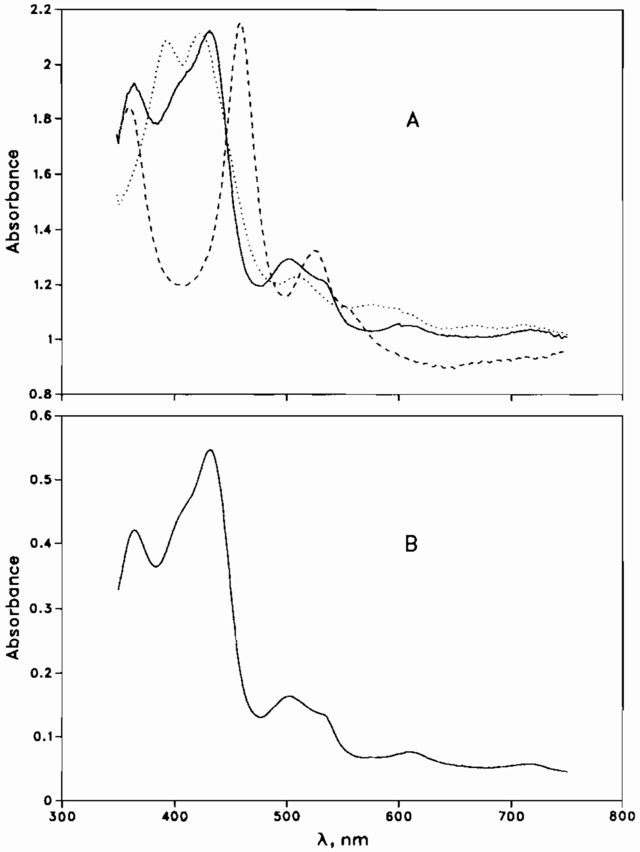

Fig. 2. (A) Thin layer visible spectroelectrochemical spectra obtained during the electrolysis of Fe(TPP)(Cl). Product formed at the $Fe(TPP)^-$ (dotted) and the $Fe(TPP)^{2-}$ (solid) potentials in DMF with tetrabutylammonium perchlorate. Product formed at the $Fe(TPP)^{2-}$ potential in DMF with sodium perchlorate (dashed). (B) Visible spectra of chemically generated $Fe(TPP)(butyl)^-$ in THF.

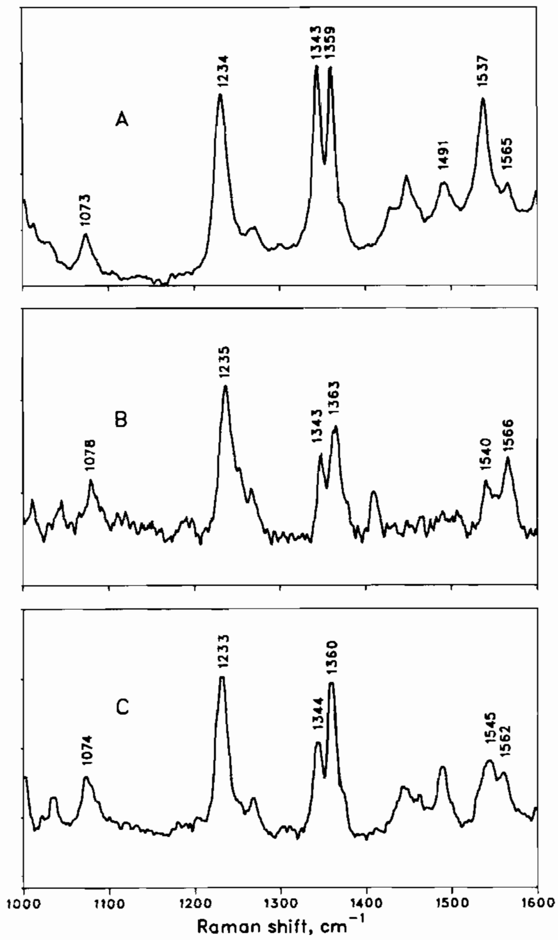

Fig. 3. Resonance Raman spectra obtained with frozen solutions: (A) Fe(TPP)(methyl); (B) $Fe(TPP)(butyl)^-$; (C) electrolysis product at −2.29 V vs. $Ag/AgNO_3$ with 0.10 M TBAP. Solvent: THF. Excitation wavelength: 413 nm. Laser power: 4 mW.

nitrosyl complex (1366 cm^{-1}), and somewhat higher than the five-coordinate high-spin complex, $Fe(TPP)(OH)^-$, which appears at 1360 cm^{-1}.

The resonance Raman spectra of Fe^{III}(TPP)(butyl) and Fe^{III}(TPP)(methyl) were very difficult to obtain due to the photodecomposition process, even in the frozen state. The methyl complex yielded a somewhat better spectrum. The results were consistent with the earlier work in benzene [24], with the ν_2 band at 1565 cm^{-1} (1563 cm^{-1} in benzene) and the ν_4 band at 1359 cm^{-1} (1363 cm^{-1} in benzene). While the ν_4 band was similar to the Fe(TPP)(Cl) value (1365 cm^{-1}), the ν_2 band was significantly higher (1565 versus 1556 cm^{-1}). The ν_2 and ν_4 bands of the ferric and ferrous alkyl complexes were relatively similar, with the values for the ferric complex occurring slightly lower in both cases. There were other spectral differences, though, between the two complexes as can be seen in Fig. 3. In particular, the ferric complex also had prominent bands at 1448 and 1491 cm^{-1}, which were not observed in the ferrous complex. The use of isotopically labelled ^{54}Fe porphyrins did not lead to any isotopically sensitive bands for either oxidation state, even in the low frequency region. Therefore, it appears that the Fe–C band is not resonance enhanced in these complexes.

The electrolysis product, which had a visible spectrum that was clearly $Fe(TPP)(R)^-$ (Fig. 2(B)), gave a resonance Raman spectrum that showed the presence of the iron alkyl structure, with a ν_4 band at 1562 cm^{-1} (Fig. 3(C)). The photoproduct band appeared at 1545 cm^{-1} and was broader than the bands in Fig. 3(A) and (B). In addition, the intensity of 1360 cm^{-1} is much higher than would be anticipated based on the intensity of the 1562 cm^{-1} band. A likely explanation may be that the photoproduct in the electrolysis product is $Fe(TPP)(OH)^-$, rather than Fe(TPP). $Fe(TPP)(OH)^-$ has bands at 1360 and 1546 cm^{-1}, which would account for the band shifts and intensities observed. Hydroxide would be readily generated under electrolysis conditions by the catalyzed reduction of trace water from the electrolyte. The presence of hydroxide would also explain the poorer stability of the electrogenerated $Fe(TPP)(R)^-$ complex in the reso-

Table 3
Resonance Raman spectra of iron porphyrin alkyl complexes

Complex	Solvent	Oxidation state/spin state	ν_4 (cm^{-1})	ν_2 (cm^{-1})	Ref.
Fe(TPP)(butyl)$^-$	THF	II/l.s.	1363	1566	this work
Fe(TPP)(butyl)	THF	III/l.s.	1364	1558	this work
Fe(TPP)(methyl)$^-$	THF	II/l.s.	1364	1565	this work
Fe(TPP)(methyl)	THF	III/l.s.	1359	1565	this work
	benzene	III/l.s.	1363	1563	[24]
Coulometry product	THF		1363	1562	this work
Fe(TPP)(Cl)	THF	III/h.s.	1365	1556	[25]
	CH_2Cl_2	III/h.s.	1366	1555	[26]
Fe(TPP)	THF	II/h.s.	1345	1540	[27]
	CH_2Cl_2	II/i.s.	1370	1565	[26]
Fe(TPP)(OH)$^-$	THF	II/h.s.	1360	1546	[27]
Fe(TPP)(NO)	THF	II/l.s.	1366	1564	[27]
Fe(TPP)(CCl_2)		II/l.s.	1369	1571	[28]
Fe(TPP)$^-$	DMF	I/l.s.	1356	1554	[29]

nance Raman, as compared to the chemically generated species. The presence of OH^- would certainly make the cleavage of the Fe–C bond easier (or recombination less likely).

The mechanism for the alkylation reaction can be visualized as an electron transfer (ET) or a nucleophilic attack (S_N2) process. These reaction mechanisms were studied extensively by Lexa et al. [11] for the reaction of iron('0') porphyrins or aromatic anion radicals with alkyl bromides. These mechanisms differentiate themselves in the degree of bond formation in the transition state. In general, the ET pathway predominates over the S_N2 pathway at high temperatures, and steric hindrance favors the ET pathway by inhibiting the S_N2 process. The S_N2 pathway was predominant for the reaction of Fe('0')(TPP) with n-butyl bromide, but the ET pathway was favored for the reaction of Fe('0')(ETIO) with t-butyl bromide [11] (ETIO = etioporphyrin). By analogy, the reaction with tetrabutylammonium ion with Fe('0')(TPP) should be quite sterically hindered, so the ET pathway should be favored, but additional evidence with regard to the activation parameters would be necessary to unequivocally determine this.

4. Conclusions

Iron('0') porphyrins can be generated chemically, and the complex is quite stable if protected from air and moisture. However, when a supporting electrolyte such as tetrabutylammonium ion was present, an alkylation reaction occurred which led to a σ-alkyl iron porphyrin. This reaction severely lowers the stability of the iron('0') complex under electrochemical conditions, and makes it impossible to study these materials using conventional spectroelectrochemical methods. Fortunately, this reaction is too slow to affect normal voltammetric studies. As part of this work, the resonance Raman spectra of σ-alkyl ferric and ferrous porphyrins were examined. No evidence was found for an isotopically sensitive Fe–C band. The ferrous complex was the most stable under laser irradiation, and the spectrum was consistent with a low-spin ferrous complex. The identity of the alkyl group cannot be unambiguously determined from the visible or the resonance Raman spectra. Because the σ-alkyl iron complex can only be observed when tetraalkylammonium salts are present, it strongly suggests that they are the alkylating agent. Further work will be necessary to verify this conclusion. No reaction was observed between iron(I) prophyrins and the supporting electrolyte. Based on the results of previous studies the most likely mechanism for the alkylation reaction is an ET mechanism where the initial step in the reaction is the transfer of an electron from the iron('0') porphyrin to the tetraalkylammonium ion. Such a direct reaction has been observed at a gold electrode [4]. Further studies are in progress to verify this mechanism.

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