

σ -Alkyl Iron Porphyrins from Sterically Encumbered Alkyl Halides and Iron("0") Porphyrins. Stabilities of the Four Accessible Oxidation States

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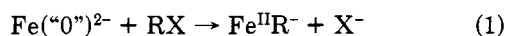
Reaction of electrochemically generated iron("0") porphyrins with alkyl halides allows one to obtain the σ -alkyl complexes with sterically hindered carbon and/or iron reacting centers. Secondary and tertiary alkyl complexes are thus easily formed directly under their most stable iron(II) oxidation state. These complexes are difficult or even impossible to obtain by the other usual methods because the initially formed σ -alkyl iron(III) complex is unstable, decomposing into the alkyl radical and the iron(II) porphyrin. Two other oxidation states, iron("I") and iron("IV"), of the σ -alkyl complexes are easily generated by electrochemical means. Their stabilities, as well as that of the σ -alkyl iron(II) complexes, are discussed as a function of the alkyl group and of the porphyrin ring and are related to the standard potentials of the redox couples involved in the reaction.

Four routes to σ -alkyl and aryl iron porphyrins have been described so far: reaction of iron(III) porphyrins with carbanion sources, usually Grignard reagents,¹ reaction of iron(II) porphyrins with alkyl radicals, reaction of iron(I) porphyrins with alkyl³ or aryl⁴ halides, and reaction of iron("0") porphyrins with alkyl halides.⁵ Several aryl and primary alkyl complexes have been obtained by using one or the other of these methods. To our knowledge, the formation of tertiary alkyl iron porphyrins has not hitherto been described. We show, in the following, that in spite of steric hindrance at the reacting carbon, these complexes can be obtained by reaction of electrochemically generated iron("0") porphyrins with the corresponding alkyl halides. It will be also shown that the reaction likewise allows the generation of σ -alkyl complexes of iron porphyrins in which the iron center is severely encumbered sterically. The reaction of iron("0") states with alkyl halides yields directly the σ -alkyl iron(II) porphyrins. Three other oxidation states of these complexes are readily obtained by electro-

chemical means, allowing one to determine the standard potential at which they are formed. Their stability is a function of the nature of the alkyl group and of the porphyrin ring. As shown in the following, they can be related to the standard potential characterizing their formation from the next oxidation state. The various iron porphyrins investigated in this work together with their conventional designation are shown in Figure 1.

Results and Discussion

σ -Alkyl Iron(II) Porphyrins from the Reaction of Alkyl Halides with Iron("0") Porphyrins in the Case of Sterically Hindered Reactants. Figure 2 shows a typical example of the reaction of an electrochemically generated iron("0") porphyrin with *sec*-BuBr. In the absence of the alkyl halide, the cyclic voltammogram of the Fe(III) porphyrin exhibits three successive one-electron reversible waves, denoted as 1/1', 2/2', and 3/3' featuring the successive formation of the Fe(II), Fe(I)⁻, and Fe("0")²⁻ complexes. The fact that all waves are reversible, even when the potential is first scanned anodically and then cathodically starting from a potential beyond the most negative wave, shows that all oxidation states, even the lowest one, are stable at least during minutes. The experiment was then repeated with presence of *sec*-BuBr. In order to investigate its reaction with Fe("0")²⁻ rather than with Fe(I)⁻, a small amount of *sec*-BuBr was introduced in the solution, small enough for not reacting appreciably with the iron(I) porphyrin at a potential negative to the 2/2' wave, during the time (minutes) in which the starting potential of the scan is set up at this value. Under these conditions, if the starting potential is located beyond the 3/3' wave, the formation of the σ -alkyl complex manifests itself by a loss of reversibility of the 3/3' wave (wave 3' decreases indicating the disappearance of the Fe("0")²⁻ complex) and by the appearance of three new waves:^{5a} 4/4', 5/5', and 6'. 5' corresponds to the oxidation of the initially formed Fe^{II}R⁻ complex into Fe^{III}R, 4, its reduction into Fe^IR²⁻, and 6', the oxidation of Fe^{III}R formed at wave 5' into Fe^{IV}R⁺ (at least transitorily). The 5/5' wave is almost reversible at 0.1 V·s⁻¹ and can be made fully reversible by raising slightly the sweep rate. This indicates that the Fe^{II}R⁻ complex formed from the reaction of *sec*-BuBr with the iron("0") porphyrin



(1) (a) Clarke, D. A.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Chem. Commun.* 1966, 208. (b) Clarke, D. A.; Dolphin, D.; Grigg, R.; Johnson, A. W.; Pinnock, H. A. *J. Chem. Soc. C* 1968, 881. (c) Ogoshi, H.; Setsuno, J.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* 1975, 97, 6461. (d) Ortiz de Montellano, P. R.; Kunze, K. L.; Augusto, A. *J. Am. Chem. Soc.* 1982, 104, 3545. (e) Mansuy, D.; Battioni, J. P. *J. Chem. Soc., Chem. Commun.* 1982, 638. (f) Ogoshi, H.; Sugimoto, H.; Yoshida, Z.; Kobayashi, H.; Sakai, H.; Maeda, Y. *J. Organomet. Chem.* 1982, 234, 185. (g) Cocolios, P.; Laviron, E.; Guillard, R. *J. Organomet. Chem.* 1982, 228, C 39. (h) Battioni, J. P.; Lexa, D.; Mansuy, D.; Savéant, J. M. *J. Am. Chem. Soc.* 1983, 105, 207. (i) Cocolios, R.; Lagrange, G.; Guillard, R. *J. Organomet. Chem.* 1983, 253, 65.

(2) Brault, D.; Neta, P. *J. Phys. Chem.* 1982, 86, 3405.

(3) (a) Lexa, D.; Mispelter, J.; Savéant, J. M. *J. Am. Chem. Soc.* 1981, 103, 6806. (b) The Fe^{III}R complex is formed in a first stage from the electrochemically generated iron(I) porphyrin (Fe(I)⁻ + RX → Fe^{III}R + X⁻) but is immediately reduced into the Fe^{II}R⁻ complex, at the electrode or by the iron(I) porphyrin in solution, since the standard potential of the Fe^{III}R/Fe^{II}R⁻ couple is positive of that of the Fe(II)/Fe(I)⁻ couple.

(4) (a) Lexa, D.; Savéant, J. M. *J. Am. Chem. Soc.* 1982, 104, 3503. (b) In this reaction, the starting aryl halide does not function directly as the electrophile. It has to be converted first, by the transfer of one electron from the electrode or from a reducing solution species, into the aryl radical which is then the actual electrophile. The reaction is thus an electrochemically catalyzed^{4c} S_{RN}1^{4d} aromatic nucleophilic substitution:^{4a} ArX + e⁻ = ArX^{-•}; ArX^{-•} → Ar[•] + X⁻; Ar[•] + Fe(I)⁻ → Fe^{II}Ar[•]; Fe^{II}Ar[•] - e⁻ = Fe^{III}Ar. (c) Savéant, J. M. *Acc. Chem. Res.* 1980, 13, 323. (d) Bunnet, J. F. *Acc. Chem. Res.* 1978, 11, 413.

(5) (a) Lexa, D.; Savéant, J. M.; Wang, D. L. *Organometallics* 1986, 5, 1428. (b) It is remarkable that in spite of reasonable spectroscopic evidence for the dominant resonance form of iron("0") porphyrins to be an iron(I) anion radical, alkylation takes place at iron only and not at the porphyrin ring as expected for an organic aromatic anion radical.^{5a}

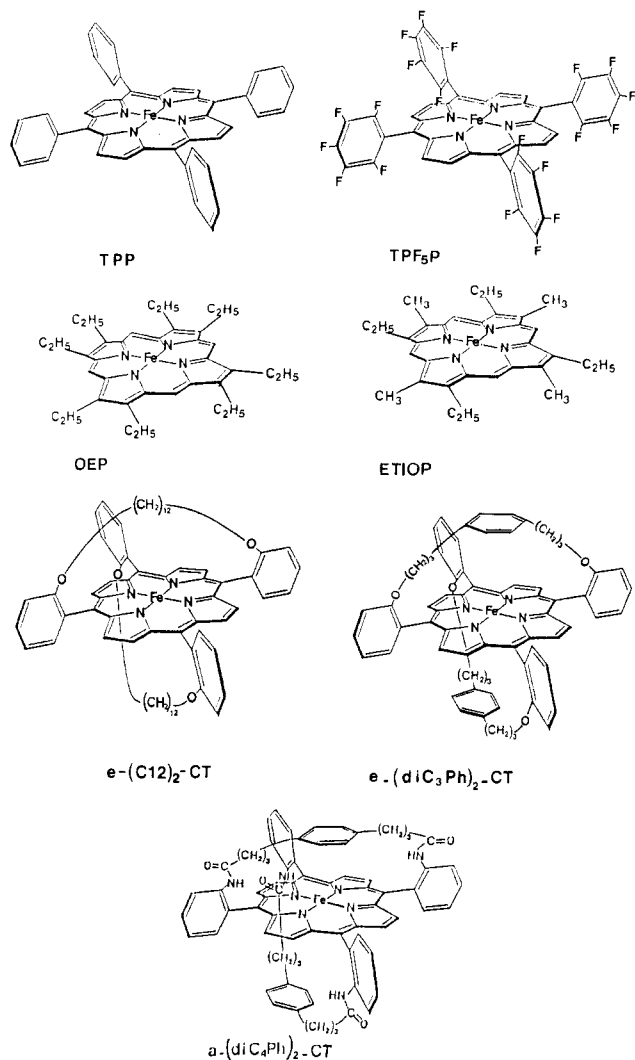


Figure 1. Iron porphyrins investigated in this work.

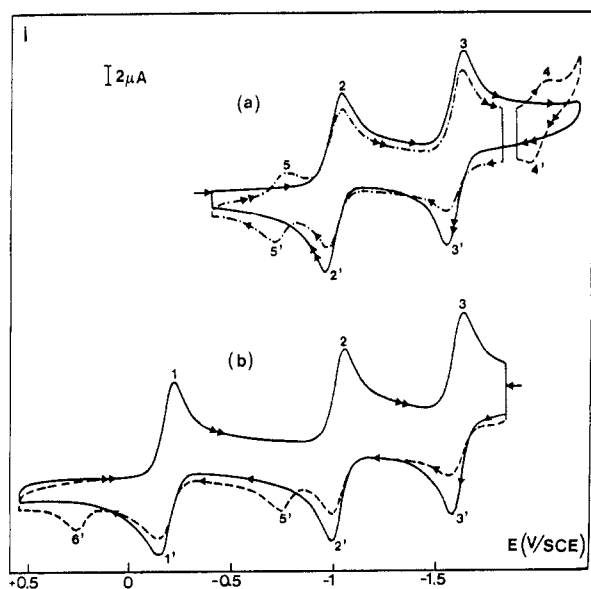


Figure 2. Cyclic voltammetry of (TPP)Fe^{III}Cl (0.73 mM) in DMF + 0.1 M NEt₄ClO₄ at 10 °C in the absence (—) and presence of 0.71 mM *sec*-BuBr (---) and (-·-·). Sweep rate = 0.1 V·s⁻¹.

is stable during at least minutes, whereas the Fe^{III}R complex obtained by oxidation of the Fe^{II}R⁻ complex is less stable, its lifetime being of the order of tens of seconds. The reason why the cyclic voltammetric scan was started

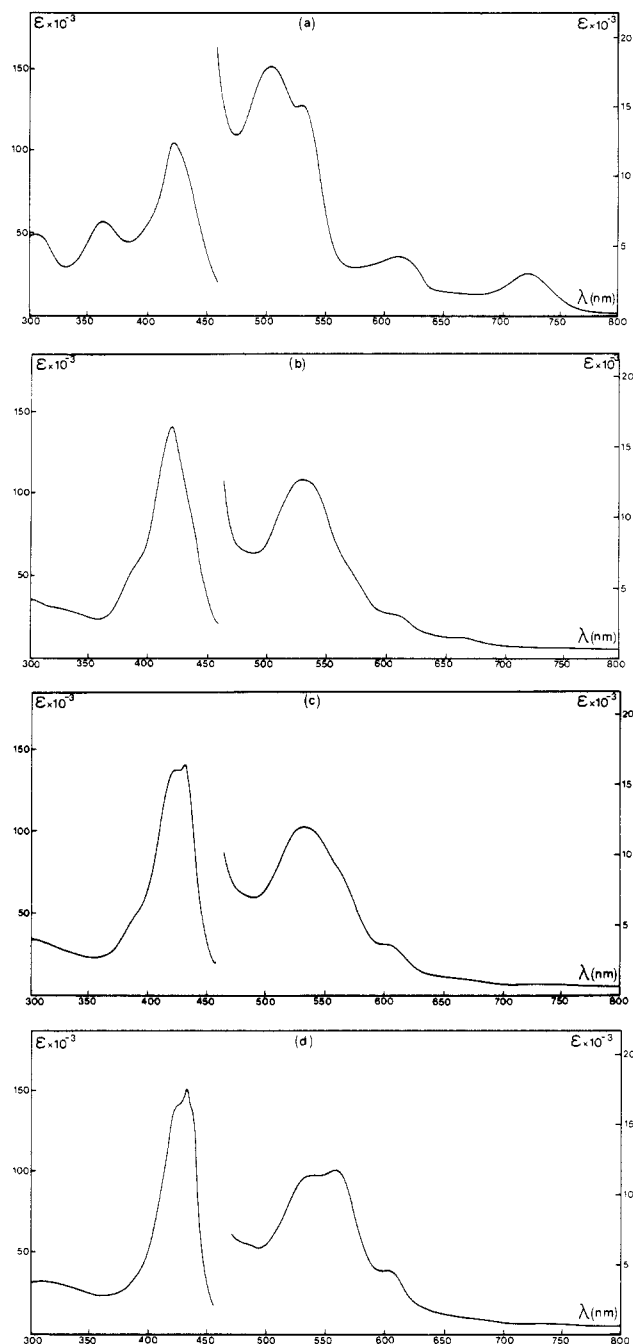


Figure 3. Thin-layer spectroelectrochemistry of (e-(C₁₂)₂-CT-TPP)Fe^{III}Cl (0.1 mM) in the presence of *sec*-BuBr (9.15 mM) at a reticulated glassy carbon grid electrode in DMF + 0.1 M NEt₄ClO₄: (a) spectrum obtained at -1.95 V vs SCE from the reaction of Fe(⁰)²⁻ with *sec*-BuBr; (b) reoxidation at -0.6 V vs SCE showing the Fe^{III}*sec*-Bu; (c) same conditions as (b) after 4 min; (d) same conditions as (b) and (c) after 10 additional min, showing the Fe(II) porphyrin spectrum.

beyond the 3/3' wave rather than in front of the 1/1' wave is that a larger amount of the reaction product, here the Fe^{II}R⁻ complex, is formed in the former than in the latter case, giving rise to higher and more distinct waves. The same strategy has been adopted throughout the work.

This is confirmed by thin-layer UV-vis spectroelectrochemical experiments. In the presence of *sec*-BuBr concentrations sufficiently small for not reacting with the iron(I) porphyrin within the time scale of the experiment (tens of minutes), a spectrum almost identical (Figure 3a) to that obtained previously for *n*-Bu iron(II) porphyrins^{5a} appears upon electrolysis at a potential slightly beyond wave 3. Reoxidation at a potential slightly positive to wave

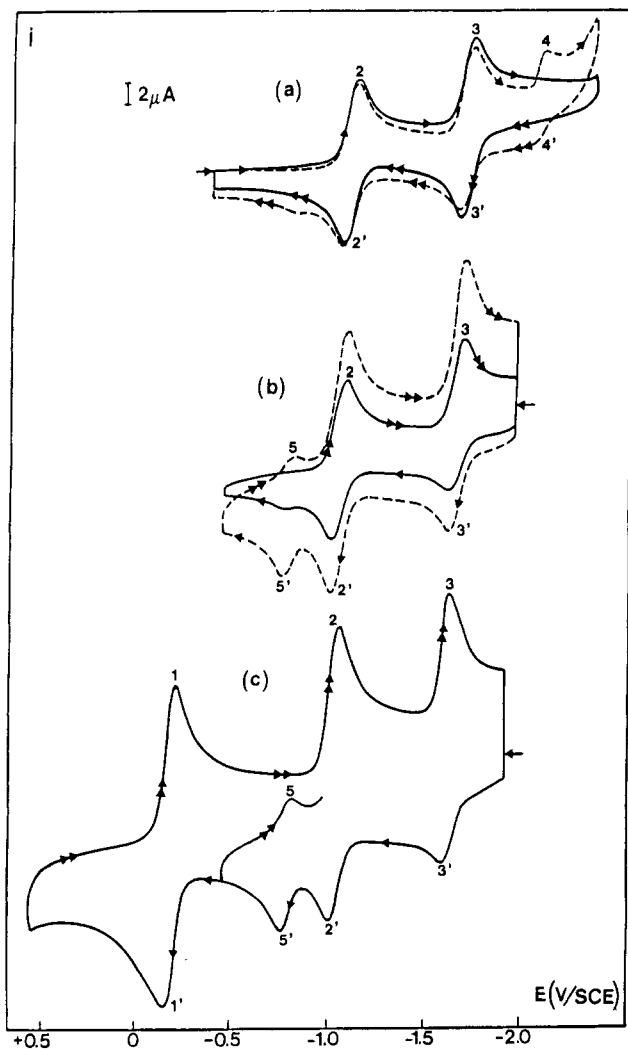


Figure 4. Cyclic voltammetry of $(\text{TPP})\text{Fe}^{\text{III}}\text{Cl}$ (0.77 mM) in DMF + 0.1 M NEt_4ClO_4 at 10 °C upon addition of *t*-BuBr: (a) *t*-BuBr concentration 0 (—), 0.44 mM (---) (sweep rate = 0.1 $\text{V}\cdot\text{s}^{-1}$); (b) *t*-BuBr concentration, 2.22 mM (sweep rate = 0.1 $\text{V}\cdot\text{s}^{-1}$ (—), 0.3 $\text{V}\cdot\text{s}^{-1}$ (---)); (c) *t*-BuBr concentration 2.22 mM (sweep rate = 0.5 $\text{V}\cdot\text{s}^{-1}$).

5' shows a transient spectrum almost identical with that obtained previously for *n*-Bu iron(III) porphyrins^{5a} which disappears rapidly at the benefit of the iron(II) porphyrin spectrum (Figure 3b-d).

Similar cyclic voltammetry experiments, carried out with *t*-BuBr, are shown in Figure 4. The formation of the σ -alkyl complex again manifests itself by the loss of reversibility of the 3/3' couple and by the appearance of waves 4 and 5'. The 5/5' couple is less reversible than in the preceding case, wave 5 requiring higher sweep rates to appear as a result of the greater instability of the $\text{Fe}^{\text{III}}\text{R}$ complex. This is also the reason why wave 6' does not appear, in contrast to what is observed with *sec*-BuBr and also *n*-BuBr.^{5a} We will see later on that, at lower temperature, wave 6' does appear, together with better reversibility of wave 5/5' owing to the ensuing stabilization of the $\text{Fe}^{\text{III}}\text{R}$ complex. Accordingly, thin-layer spectroelectrochemistry at a potential slightly beyond wave 3 shows full formation of the σ -alkyl iron(II) porphyrin, but reoxidation at a potential slightly positive to wave 5' shows merely the iron(II) porphyrin spectrum with no appearance of the σ -alkyl iron(III) porphyrin spectrum.

The same results were obtained with the other simple porphyrins TPF₅P, ETIOP, and OEP (Figure 1). To test the possibility of obtaining the σ -alkyl complexes with a

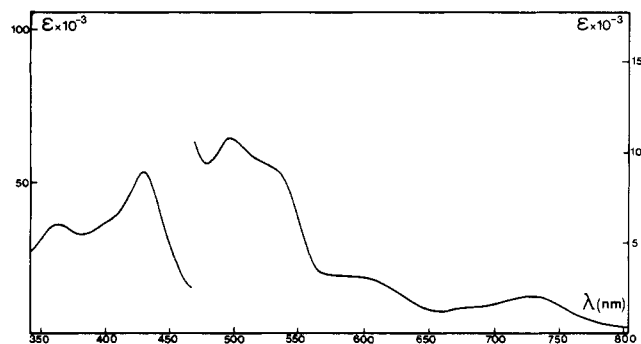


Figure 5. Thin-layer spectroelectrochemistry of $(a-(\text{diC}_4\text{Ph})_2\text{-CT-TPP})\text{Fe}^{\text{III}}\text{Cl}$ (0.18 mM) in the presence of *t*-BuBr (1.8 mM) in DMF + 0.1 M NEt_4ClO_4 on a platinum grid electrode at -1.6 V vs SCE showing the spectrum of $\text{Fe}^{\text{II}}\text{R}^-$ formed from the reaction of $\text{Fe}^{\text{("0")2-}}$ and *t*-BuBr.

sterically hindered iron center, we investigated the reaction of the basket-handle porphyrin $(e-(\text{diC}_3\text{Ph})_2\text{-CT-TPP})\text{Fe}^{\text{("0")2-}}$ (Figure 1) with *n*-BuBr by cyclic voltammetry and spectroelectrochemistry. It was found that both the $\text{Fe}^{\text{II}}\text{R}^-$ and $\text{Fe}^{\text{III}}\text{R}$ complexes are sufficiently stable, in spite of the strong steric hindrance caused by the presence of the phenyl groups in the basket handles, to appear in cyclic voltammetry. In spectroelectrochemistry, the $\text{Fe}^{\text{II}}\text{R}^-$ complex appears as stable whereas the $\text{Fe}^{\text{III}}\text{R}$ complex disappears after ca. 10 min. In order to investigate an even more sterically hindered system, we carried out the same experiments with the basket-handle porphyrin $(a-(\text{diC}_4\text{Ph})_2\text{-CT-TPP})\text{Fe}^{\text{("0")2-}}$ and *t*-BuBr. The $\text{Fe}^{\text{II}}\text{R}^-$ complex does appear both in cyclic voltammetry and spectroelectrochemistry (Figure 5), but the $\text{Fe}^{\text{III}}\text{R}$ complex is too unstable to be observed in one or the other experiments.

We also found, in several cases, that the stability of the $\text{Fe}^{\text{II}}\text{R}^-$ complexes is sufficient for this compound to be obtained in a preparative scale cell and further characterized spectroscopically after transfer of the solution to a standard spectrometric cell, meaning that its lifetime is of the order of 1 h or more.

From the preceding, we conclude that the σ -alkyl iron(II) complexes are readily formed by reaction of iron ("0") porphyrins with alkyl halides, even in the case of strong steric hindrance at the carbon and/or iron centers. The rate constant of the reaction is a function of the nature of the alkyl halide and of the porphyrin structure. A detailed study of the kinetics of the reaction as a function of these structural effects has been published elsewhere.⁶ It shows that in the absence of steric constraints the reaction is of the $\text{S}_{\text{N}}2$ type. Bonding interactions in the transition state are then strong enough to make the iron("0") porphyrin react as an inner-sphere electron donor rather than as an outer-sphere electron donor. Bonding stabilization of the transition state is weakened and eventually annihilated by steric hindrance at the carbon and/or iron center. In the rate-determining step, the iron("0") porphyrin then tends to react as an outer-sphere electron donor, electron transfer to the alkyl halide being concerted with the cleavage of the carbon-halogen bond. The formation of the σ -alkyl iron(II) complex takes place in a successive step from the coupling of the iron atom and the alkyl radical. The examples of sterically hindered systems described above follow this "ET" mechanism.⁶ It is remarkable that the steric constraints, although sufficient for annihilating the bonding interactions in the

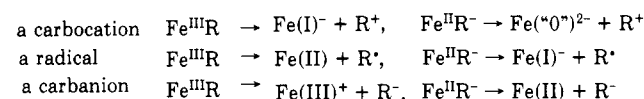
Table I. Characteristic Standard Potentials

porphyrin	Fe ^{II} /Fe ^I	Fe ^I /Fe ^{•0.2-}	Fe ^{III} R/Fe ^{II} R ⁻	Fe ^{II} R/Fe ^{•I} R ²⁻	Fe ^{III} R/Fe ^{II} R ⁻	Fe ^{II} /Fe ^I	Fe ^I /Fe ^{•0.2-}
	a, g	a, g	a, g	a, g	Fe ^{III} R/Fe ^{II} R ⁻ b, g	Fe ^{II} R/Fe ^{•I} R ²⁻ b, g	Fe ^{II} R/Fe ^{•I} R ²⁻ b, g
R = <i>n</i> -Bu (20 °C)							
TPF ₅ P	-0.78 ₃	-1.25 ₈	-0.51 ₅	-1.59 ₄	26 ₈	81 ₁	33 ₆
TPP ^f	-0.98 ₃	-1.60 ₅	-0.73 ₆	-1.95 ₆	25 ₂	95 ₈	35 ₁
OEP ^f	-1.20 ₀	-1.87 ₈	-0.99 ₇	-2.25 ₀	20 ₈	104 ₇	37 ₂
ETIOP	-1.21 ₆	-1.87 ₀	-1.00 ₁	-2.27 ₀	21 ₅	105 ₄	40 ₀
a-(diC ₄ Ph) ₂ -CT-TPP	-0.90 ₀	-1.50 ₅	-0.63 ₀	-1.76 ₅	27 ₀	85 ₇	26 ₀
a-(C ₁₂) ₂ -AC-TPP ^f	-0.90 ₆	-1.46 ₆	-0.58 ₃	-1.69 ₆	32 ₃	79 ₀	23 ₀
a-(C ₁₂) ₂ -CT-TPP ^f	-0.93 ₆	-1.53 ₅	-0.63 ₃	-1.81 ₁	30 ₃	87 ₅	27 ₆
e-(diC ₃ Ph) ₂ -CT-TPP	-1.02 ₃	-1.80 ₇	-0.92 ₂	<i>d</i>	10 ₈	<i>d</i>	<i>d</i>
e-(C ₁₂) ₂ -CT-TPP	-1.12 ₀	-1.94 ₇	-0.94 ₀	<i>d</i>	18 ₀	<i>d</i>	<i>d</i>
R = <i>sec</i> -Bu (10 °C)							
TPF ₅ P	-0.79 ₄	-1.26 ₃	-0.50 ₀	-1.61 ₀	29 ₄	81 ₆	34 ₇
TPP	-1.01 ₀	-1.59 ₅	-0.76 ₀	-1.97 ₇	25 ₀	96 ₇	38 ₅
ETIOP	-1.22 ₁	-1.86 ₇	-1.02 ₃	<i>d</i>	19 ₃	<i>d</i>	<i>d</i>
R = <i>t</i> -Bu (10 °C)							
TPF ₅ P	-0.79 ₄	-1.26 ₃	-0.49 ₄	-1.58 ₂	30 ₀	78 ₈	31 ₉
TPP	-1.01 ₀	-1.59 ₁	-0.76 ₄	-1.95 ₁	24 ₆	94 ₁	35 ₉
OEP	-1.21 ₀	-1.86 ₅	-1.02 ₃	-2.287 ₀ ^e	18 ₈	107 ₀	41 ₃
ETIOP	-1.22 ₁	-1.86 ₇	-1.04 ₂	<i>d</i>	17 ₉	<i>d</i>	<i>d</i>
a-(diC ₄ Ph) ₂ -CT-TPP	-0.88 ₇	-1.47 ₅	>-0.89 ₀ ^c	-1.76 ₀	>29 ₇	87 ₃	28 ₅

^aIn V vs SCE. ^bIn mV. ^cWave 5' is irreversible. ^dWave 4 is irreversible. ^eAt 100 V·s⁻¹. ^fFrom ref 5a. ^gSubscript digit indicates that the potential determinations are accurate within a few millivolts.

transition state, are not strong enough to impede the formation of the σ -alkyl iron(II) complex as the final product.

Stability of the σ -Alkyl Iron(III) Porphyrins. The stability of the σ -alkyl Fe(III) porphyrin depends both on the nature of the alkyl group and of the porphyrin ring. The results described above show unambiguously that the σ -alkyl complexes are less stable in their Fe(III) than in their Fe(II) oxidation state. Three modes of breaking of the iron-carbon bond in the Fe^{III}R and Fe^{II}R⁻ complexes can be envisaged involving the formation of



The first of these possible modes of decomposition is quite unlikely since the difference in driving forces (DF) between the carbocation and the radical modes

$$\text{DF}^{\text{R}^\bullet}_{\text{Fe}^{\text{III}}\text{R}} - \text{DF}^{\text{R}^+}_{\text{Fe}^{\text{III}}\text{R}} = E^0_{\text{R}^+/\text{R}^\bullet} - E^0_{\text{Fe}(\text{II})/\text{Fe}(\text{I})^-}$$

$$\text{DF}^{\text{R}^\bullet}_{\text{Fe}^{\text{II}}\text{R}^-} - \text{DF}^{\text{R}^+}_{\text{Fe}^{\text{II}}\text{R}^-} = E^0_{\text{R}^+/\text{R}^\bullet} - E^0_{\text{Fe}(\text{I})^-/\text{Fe}(\text{I})^{\bullet 0.2-}}$$

is certainly much in favor of the later in both cases. The R⁺/R[•] couple is indeed largely positive⁷ of both the Fe(II)/Fe(I)⁻ and the Fe(I)⁻/Fe(I)^{•0.2-} couples.

As to the carbanion mode

$$\text{DF}^{\text{R}^-}_{\text{Fe}^{\text{III}}\text{R}} - \text{DF}^{\text{R}^-}_{\text{Fe}^{\text{II}}\text{R}^-} = E^0_{\text{Fe}(\text{III})^+/\text{Fe}(\text{II})} - E^0_{\text{R}^-\text{R}^\bullet}$$

$$\text{DF}^{\text{R}^-}_{\text{Fe}^{\text{II}}\text{R}^-} - \text{DF}^{\text{R}^-}_{\text{Fe}^{\text{II}}\text{R}^-} = E^0_{\text{Fe}(\text{II})/\text{Fe}(\text{I})^-} - E^0_{\text{R}^-\text{R}^\bullet}$$

Approximate estimations of $E^0_{\text{R}^-\text{R}^\bullet}$ exist for *n*-Bu, *sec*-Bu, and *t*-Bu: in DMF at 10 °C, ≤ -1.4 (*n*-Bu), -1.5 (*sec*-Bu), and -1.6 (*t*-Bu) V vs SCE.⁸ The uncertainty on these values is about ± 0.2 V, and the value for *n*-Bu is most probably not more than 0.1–0.2 V positive of -1.4 . There

(7) (a) For example with R = 9-mesitylfluorene the standard potential of the R⁺/R[•] couple is 0.75 V vs SCE in acetonitrile.^{7b} With R = PhCH₂, Ph₂CH, and PhC(CH₃)₂ it is larger or equal to 0.734, 0.354, and 0.134 V vs SCE, respectively.^{7c} (b) Andrieux, C. P.; Merz, A.; Savéant, J. M. *J. Am. Chem. Soc.* 1985, 107, 6097. (c) Wayner, D. D. M.; Griller, D. *J. Am. Chem. Soc.* 1985, 107, 7764.

(8) Andrieux, C. P.; Gallardo, I.; Savéant, J. M. *J. Am. Chem. Soc.* 1983, 111, 1620.

is thus little doubt that the radical decomposition predominates over the carbanion decomposition in the case of Fe^{III}R. The case of Fe^{II}R⁻ is more ambiguous but also less critical since these species are stable under our experimental conditions.

In the context of a radical decomposition the lesser stability of the Fe^{III}R complex as compared to the Fe^{II}R⁻ complex parallels the standard potential difference:

$$\text{DF}^{\text{R}^\bullet}_{\text{Fe}^{\text{III}}\text{R}} - \text{DF}^{\text{R}^\bullet}_{\text{Fe}^{\text{II}}\text{R}^-} = E^0_{\text{Fe}^{\text{III}}\text{R}/\text{Fe}^{\text{II}}\text{R}^-} - E^0_{\text{Fe}(\text{II})/\text{Fe}(\text{I})^-}$$

This is indeed positive of the order of 0.2–0.3 eV (Table I). On the opposite

$$\text{DF}^{\text{R}^\bullet}_{\text{Fe}^{\text{III}}\text{R}} - \text{DF}^{\text{R}^\bullet}_{\text{Fe}^{\text{II}}\text{R}^-} = E^0_{\text{Fe}^{\text{III}}\text{R}/\text{Fe}^{\text{II}}\text{R}^-} - E^0_{\text{Fe}(\text{III})^+/\text{Fe}(\text{II})}$$

is largely negative, of the order of -0.6 eV, confirming the unlikelihood of this mode of decomposition.

In the framework of a radical-type decomposition, let us note that the behavior of iron and cobalt porphyrins are opposite. In the case of cobalt porphyrins, the Co^{III}R/Co^{II}R⁻ couple is negative of the Co(II)/Co(I) couple,⁹ meaning that the Co^{III}R complex is more stable toward radical decomposition than is the Co^{II}R⁻ complex. This difference is probably related to the fact that Co(II) has a radical character whereas in the case of iron, it is Fe(I)⁻ that possesses a radical character.

The radical decomposition of both the Fe^{III}R and Fe^{II}R⁻ are strongly uphill processes. The reverse reaction can thus be assumed to proceed at a rate close to the diffusion limit, i.e., ca. 10^{10} M⁻¹ s⁻¹. In the case of TPP, the rate constant for the decomposition of Fe^{III}R is of the order of 0.1 and 1 s⁻¹ for *sec*-Bu and *t*-Bu, respectively. The ratio of the dissociation rate constants of the Fe^{II}R⁻ over the Fe^{III}R complexes is thus obtained from

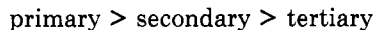
$$\frac{RT}{F} \ln \frac{k_{\text{diss}}^{\text{Fe}^{\text{II}}\text{R}^-}}{k_{\text{diss}}^{\text{Fe}^{\text{III}}\text{R}}} = \text{DF}^{\text{R}^\bullet}_{\text{Fe}^{\text{II}}\text{R}^-} - \text{DF}^{\text{R}^\bullet}_{\text{Fe}^{\text{III}}\text{R}}$$

From the data listed in Table I, $k_{\text{diss}}^{\text{Fe}^{\text{II}}\text{R}^-}$ can thus be roughly estimated as being of the order of 10^{-5} and 10^{-4} s⁻¹ for *sec*-Bu and *t*-Bu, respectively. The corresponding lifetimes are thus largely sufficient for the Fe^{II}R⁻ complex

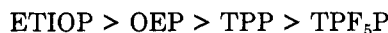
(9) Lexa, D.; Savéant, J. M.; Soufflet, J. P. *J. Electroanal. Chem.*, 1979, 100, 159.

to be obtained in the time scale of cyclic voltammetry, thin-layer spectroelectrochemistry, and even preparative-scale electrolysis.

From the variations of the cyclic voltammograms with sweep rate, we found that the stability of the $\text{Fe}^{\text{III}}\text{R}$ complex varies with the alkyl group, in the order



and with the porphyrin ring (Figure 1) in the order



The standard potential difference $E^0_{\text{Fe}^{\text{III}}\text{R}/\text{Fe}^{\text{II}}\text{R}^-} - E^0_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}}$ (Table I) remains about the same, given the porphyrin ring, when going from *n*-Bu to *sec*-Bu and *t*-Bu, indicating a concomitant decrease of the stabilities of both the $\text{Fe}^{\text{III}}\text{R}$ and $\text{Fe}^{\text{II}}\text{R}^-$ complexes. Steric hindrance has been shown to slow down the formation of $\text{Fe}^{\text{II}}\text{R}^-$ from the reaction of $\text{Fe}^{\text{II}}(\text{O})^{2-}$ with the alkyl halide, but it has no reason to influence the stabilities of $\text{Fe}^{\text{II}}\text{R}^-$ and $\text{Fe}^{\text{III}}\text{R}$ complexes, once formed. An important reason why the stabilities decrease from primary to secondary and tertiary alkyls is that the alkyl radical is more and more stable in the series (the free enthalpies of formation of the butyl radicals in the gas phase are 1.554 (*n*), 1.443 (*sec*), and 1.206 (*t*) eV^{10}).

It is seen from Table I that the variations of $E^0_{\text{Fe}^{\text{III}}\text{R}/\text{Fe}^{\text{II}}\text{R}^-} - E^0_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}}$ parallel those of $\text{Fe}^{\text{III}}\text{R}$ stability: electron-attracting substituents destabilize the $\text{Fe}^{\text{III}}\text{R}$ complex vis-à-vis the $\text{Fe}^{\text{II}}\text{R}^-$ complex and increase the standard potential difference and vice versa for electron-donating substituents.

The same effects also appear with the basket-handle porphyrins: the standard potential difference is significantly smaller in the ether-linked series than in the amide-linked series, due to electron donation by the ether groups in the first case and to through-space electron withdrawal by the secondary amide groups¹¹ in the second. In the case of the *n*-Bu complex of *e*-(diC_3Ph)₂-CT-TPP, the small value of the standard potential difference and the fact that the $\text{Fe}^{\text{III}}\text{R}$ complex is only moderately stable owing to steric hindrance indicate that this also significantly destabilizes the $\text{Fe}^{\text{II}}\text{R}^-$ complex. In the case of the *t*-Bu complex of *a*-(diC_3Ph)₂-CT-TPP the difference in stability between the $\text{Fe}^{\text{II}}\text{R}^-$ and $\text{Fe}^{\text{III}}\text{R}$ complexes is much larger (at least 0.3 eV) while the $\text{Fe}^{\text{III}}\text{R}$ has now a lifetime smaller than 1 s, both because of steric hindrance and of the better stability of the *t*-Bu radical as compared to the *n*-Bu radical.

Reaction of Secondary and Tertiary Alkyl Halides with Iron(I) Porphyrins. The production of σ -alkyl iron porphyrins from the reaction of iron("0") porphyrins with alkyl halides has two advantageous features. First, the reaction is fast even with sterically encumbered carbon

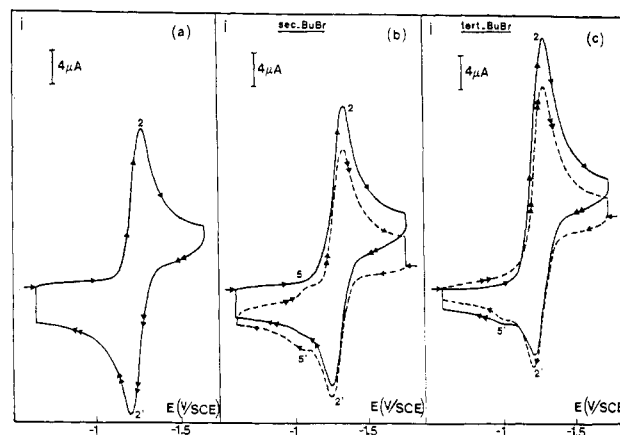
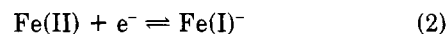


Figure 6. Cyclic voltammetry of (OEP) Fe^{II} (1 mM) in DMF + 0.1 M NET_4ClO_4 at 10 °C (sweep rate = 0.2 $\text{V}\cdot\text{s}^{-1}$): (a) in the absence of alkyl halide; (b) in the presence of 260 mM *sec*-BuBr; (c) in the presence of 183 mM of *t*-BuBr.

and/or iron centers owing to the strong electron donor properties of iron("0") porphyrins. Second, the most stable oxidation state of the σ -alkyl complex, viz. $\text{Fe}^{\text{II}}\text{R}^-$, is directly generated in a single step, another reason that makes the formation of secondary and tertiary alkyl complexes possible even in the case of sterically encumbered iron centers. Starting from the iron(I) porphyrins, the reaction is slower because they are not as good electron donors as the corresponding iron("0") porphyrins. Furthermore, the primary product of the reaction is the $\text{Fe}^{\text{III}}\text{R}$ complex which is further reduced, in a successive step into the final $\text{Fe}^{\text{II}}\text{R}^-$ complex at the potential where the reaction is carried out:¹²



The possibility of forming the alkyl complex thus depends upon the outcome of the competition between reactions 4 and 5. As found earlier, it is quite possible to obtain σ -alkyl complexes in this way in the case of primary alkyl halides,^{3a} in keeping with the good stability of the $\text{Fe}^{\text{III}}\text{R}$ complex in this case. An example of the reaction of iron(I) porphyrins with secondary and tertiary alkyl halides is shown in Figure 6.

As expected from the low reactivity of iron(I) porphyrins with sterically encumbered carbon centers⁶ only a small amount of the $\text{Fe}^{\text{II}}\text{R}^-$ complex, detectable by means of wave 5' which features its reoxidation into $\text{Fe}^{\text{III}}\text{R}$, is formed even starting the potential scan in the anodic direction from a potential located beyond the $\text{Fe}(\text{II})/\text{Fe}(\text{I})^-$ wave. Wave 5' is, however, clearly visible, attesting the formation of the $\text{Fe}^{\text{II}}\text{R}^-$ complex. In the case of *sec*-BuBr, wave 5/5' is reversible whereas it is not in the case of *t*-BuBr in keeping with the stability of the $\text{Fe}^{\text{III}}\text{R}$ complex being

(10) (a) Andrieux, C. P.; Gallardo, I.; Savéant, J. M.; Su, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 638. (b) Benson, S. W. *Thermodynamical Kinetics*, 2nd ed.; Wiley: New York, 1976. (11) (a) For a detailed discussion of the through-space effects of secondary amide groups located in the closed vicinity of the porphyrin ring on the reactivity of the iron center see ref 11b-i and ref 5a. (b) Lexa, D.; Momenteau, M.; Rentien, P.; Rytz, G.; Savéant, J. M.; Xu, F. *J. Am. Chem. Soc.* **1984**, *106*, 4755. (c) Lexa, D.; Momenteau, M.; Savéant, J. M.; Xu, F. *Inorg. Chem.* **1985**, *24*, 122. (d) Gueutin, C.; Lexa, D.; Momenteau, M.; Savéant, J. M.; Xu, F. *Inorg. Chem.* **1986**, *25*, 4294. (e) Lexa, D.; Momenteau, M.; Savéant, J. M.; Xu, F. *J. Am. Chem. Soc.* **1986**, *108*, 6937. (f) Lexa, D.; Momenteau, M.; Savéant, J. M.; Xu, F. *Inorg. Chem.* **1986**, *26*, 4857. (g) Lexa, D.; Maillard, P.; Momenteau, M.; Savéant, J. M. *J. Phys. Chem.* **1987**, *91*, 451. (h) Lexa, D.; Momenteau, M.; Savéant, J. M.; Xu, F. *J. Electroanal. Chem.* **1987**, *237*, 131. (i) Lexa, D.; Savéant, J. M. *Supramolecular Effects in the Redox and Coordination Chemistry of Superstructured Iron Porphyrins*. In *Redox Chemistry and Interfacial Behavior of Biological Molecules*, Dryhurst, G., Ed.; Plenum: New York, 1988; pp 1-25.

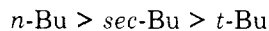
(12) (a) In the electrochemical jargon, this is an ECE process, i.e., a reaction involving a chemical step C, in the present case, the reaction of the alkyl halide with $\text{Fe}(\text{I})$, interposed between two electron-transfer steps (E). The second "E" step could be either a direct reduction at the electrode surface or a homogeneous reduction by the $\text{Fe}(\text{I})^-$ porphyrin generated at the electrode. The reason why we consider that the later reaction predominates over the former is related to the fact that the "C" reaction is slow: the $\text{Fe}(\text{III})\text{R}$ is thus formed far from the electrode surface and will be reduced by $\text{Fe}(\text{I})^-$ before it has time to reach back the electrode. For a discussion of this point on a more quantitative basis see ref 12b and references cited therein. (b) Amatore, C.; Gareil, M.; Savéant, J. M. *J. Electroanal. Chem.* **1983**, *147*, 1.

larger in the first case than in the second, as already discussed in the preceding section. Reaction 4 thus overcomes reaction 5 in the first case but not in the second. Accordingly, wave 2 appears higher with *t*-BuBr than with *sec*-BuBr in spite of the fact that reaction 3 is slower, pointing to its catalytic character. This indicates that reaction 5 is now able to produce a nonnegligible amount of Fe(II) at the expense of Fe^{II}R⁻, thus regenerating, at least partly, the starting complex which amounts to homogeneously catalyzing the electrochemical reduction of the alkyl halide at the potential of the Fe(II)/Fe(I)⁻.¹³ There is little chance to obtain the alkyl iron complex from electrogenerated Fe(I)⁻ at preparative scale in the case of tertiary alkyl halides in spite of the fact that the expected product, i.e., Fe^{II}R⁻, is stable. In such cases, the reaction with iron("0") porphyrins is obviously superior since it yields the Fe^{II}R⁻ complex directly in a one-step process.

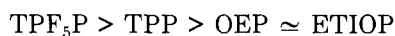
σ -Alkyl Iron("I") and Iron("IV") Porphyrins. Waves 4 and 6' (Figures 2 and 4) indicate the possibility of forming, at least transiently, the Fe^IR²⁻ and Fe^{IV}R⁺ complexes (formal oxidation states), respectively.

Reversibility can be reached for wave 4 at moderate sweep rates (below 1 V·s⁻¹) in most cases, indicating that the Fe^IR²⁻ oxidation state can be observed within the time scale of cyclic voltammetry. It is, however, too unstable to be observed in thin-layer spectroelectrochemistry and under preparative scale conditions. These observations were made for small concentrations (in the millimolar range) of added alkyl halides. The instability of the Fe^IR²⁻ complex increases when larger concentrations of the alkyl halide are introduced in the solution, giving rise to catalytic currents.

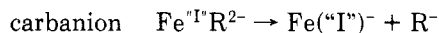
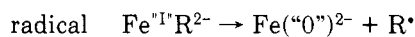
Given the porphyrin ring, the stability of the Fe^IR²⁻ complex varies in the order



Given the alkyl group, it varies as



Two modes of decomposition of the Fe^IR²⁻ complex can be envisaged leading either to the alkyl radical or the carbanion



The variation of the stability with the alkyl group would point to a radical decomposition, since *t*-Bu[·] is more stable than *sec*-Bu[·] and *n*-Bu[·], whereas this is not the case with the carbanions. As far as driving forces are concerned, clear-cut conclusions are difficult to reach.

$$\text{DF}_{\text{Fe}^{\text{I}}\text{R}^{2-}}^{\text{R}^{\cdot}} - \text{DF}_{\text{Fe}^{\text{I}}\text{R}^{2-}}^{\text{R}^{-}} = E_{\text{Fe}(\text{"0"})^{2-}/\text{Fe}(\text{"I"})^{-}}^0 - E_{\text{R}^{\cdot}/\text{R}^{-}}^0$$

may change sign as a function of the alkyl group and the porphyrin ring. As to the difference in stabilities between the Fe^IR²⁻ and Fe^{II}R⁻ complexes

$$\text{DF}_{\text{Fe}^{\text{I}}\text{R}^{2-}}^{\text{R}^{\cdot}} - \text{DF}_{\text{Fe}^{\text{II}}\text{R}^{-}}^{\text{R}^{\cdot}} = E_{\text{Fe}(\text{"0"})^{2-}/\text{Fe}(\text{"I"})^{-}}^0 - E_{\text{Fe}^{\text{II}}\text{R}^{-}/\text{Fe}^{\text{I}}\text{R}^{2-}}^0$$

$$\text{DF}_{\text{Fe}^{\text{I}}\text{R}^{2-}}^{\text{R}^{-}} - \text{DF}_{\text{Fe}^{\text{II}}\text{R}^{-}}^{\text{R}^{-}} = E_{\text{Fe}(\text{"I"})^{-}/\text{Fe}(\text{"0"})^{2-}}^0 - E_{\text{Fe}^{\text{II}}\text{R}^{-}/\text{Fe}^{\text{I}}\text{R}^{2-}}^0$$

we see that they are positive in both cases (Table I) in keeping with the greater instability of the Fe^IR²⁻ complex as compared to the Fe^{II}R⁻ complex. Upon varying the porphyrin ring the instability of the Fe^IR²⁻ as revealed by cyclic voltammetry parallels the variation of the driving

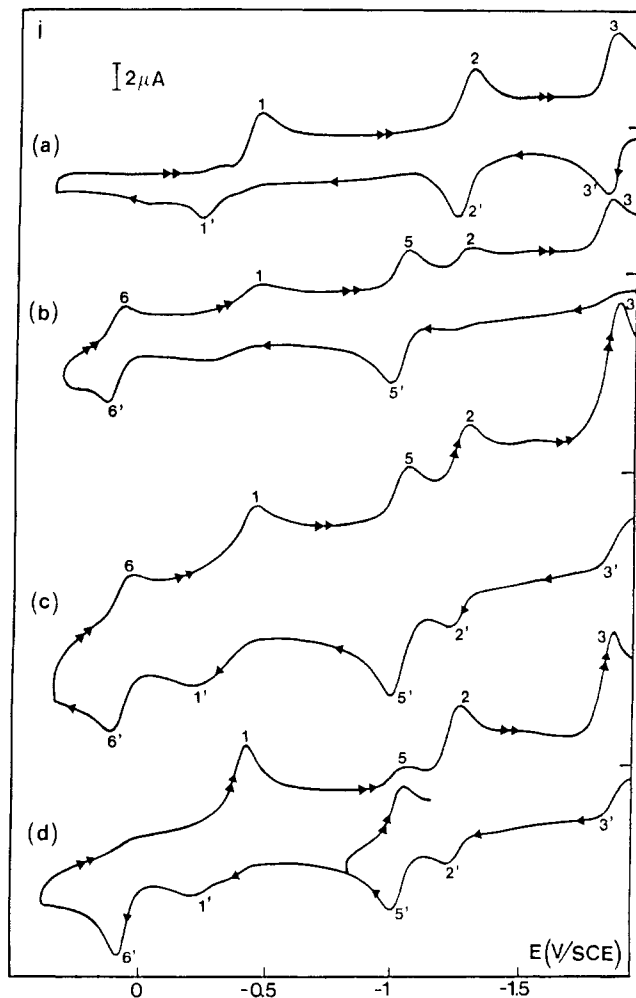


Figure 7. Cyclic voltammetry of (ETIOP)Fe^{III}Cl in DMF + 0.1 M NEt₄ClO₄ at -50 °C (sweep rate = 0.2 V·s⁻¹) in the absence of alkyl halide (a) and in the presence of 6.5 mM *n*-BuBr (b), 31.3 mM *sec*-BuBr (c), and 18 mM *t*-BuBr (d). Porphyrin concentration: a, b, d, 1 mM; c, 1.39 mM.

force differences for either the radical or the carbanion decomposition.

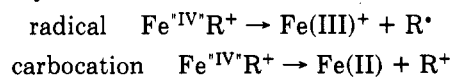
As regards now the Fe^{IV}R⁺ oxidation state of the σ -alkyl complex, it is unstable in all cases at room temperature (see ref 5a for *n*-Bu and Figures 2 and 3 for *sec*-Bu and *t*-Bu). In the case of *t*-Bu, the oxidation wave of Fe^{III}R (6') does not even appear (Figure 4) owing to the instability of the Fe^{III}R complex. Figure 7 shows the cyclic voltammograms for *n*-, *sec*-, and *t*-Bu obtained at -50 °C. Wave 6' is clearly visible in all cases including *t*-Bu (wave 5/5' is now reversible unlike what it was at room temperature) owing to the stabilization of the Fe^{III}*t*-Bu complex. With *n*-Bu and *sec*-Bu, wave 6' is reversible indicating that the Fe^{IV}R⁺ complex is sufficiently stabilized by the decrease of the temperature to appear in the time scale of cyclic voltammetry. This is not the case with *t*-Bu for which wave 6' remains irreversible.

In no case did we find that the decomposition of the Fe^{IV}R⁺ complex leads to a new wave attributable to the migration of the alkyl group from the iron to a porphyrin nitrogen as reported in the case where R is a phenyl group.¹⁴ Decomposition was always found to produce the wave system of the starting porphyrin (Figures 2, 4, and 7).

(13) For a general discussion of this type of two-step homogeneous chemical catalysis of electrochemical reaction see ref 5a.

(14) (a) Lançon, D.; Cocolios, P.; Guillard, R.; Kadish, K. M. *Organometallics* 1984, 3, 1164.

Two modes of decomposition of the $\text{Fe}^{\text{IV}}\text{R}^+$ complex can be envisaged leading to the radical and the carbocation, respectively.



They are both compatible with the observation that the $\text{Fe}^{\text{IV}}t\text{-Bu}^+$ complex is significantly less stable than the *n*-Bu and *sec*-Bu complexes, since both the radical and the carbocation are more stable in the tertiary case. The difference in driving forces between the two reactions

$$DF^{\text{R}^{\cdot}}_{\text{Fe}^{\text{IV}}\text{R}^+} - DF^{\text{R}^+}_{\text{Fe}^{\text{IV}}\text{R}^+} = E^0_{\text{R}^+/\text{R}^{\cdot}} - E^0_{\text{Fe(III)}^+/\text{Fe(II)}}$$

is largely in favor of the radical decomposition since $E^0_{\text{Fe(III)}^+/\text{Fe(II)}}$ is located between 0 and 0.5 V vs SCE whereas $E^0_{\text{R}^+/\text{R}^{\cdot}}$ is much more positive.⁷

Conclusion

Reaction of electrochemically generated iron("0") porphyrins with alkyl halides appears as an attractive route to the corresponding σ -alkyl complexes, particularly in the case where the carbon and/or iron reacting centers are strongly hindered sterically. There are two reasons for the success of this method. One is that iron("0") porphyrins are good electron donors which make them able to react rapidly as outer-sphere reagents in the cases where bonding interactions in the transition state are annihilated by steric hindrance, thus impeding an $\text{S}_{\text{N}}2$ reaction. The second reason is that the reaction leads directly to the σ -alkyl iron complex in its most stable oxidation state, namely, $\text{Fe}^{\text{II}}\text{R}^-$. The reaction thus allows one to obtain σ -alkyl iron complexes with secondary and tertiary alkyl groups, whereas this is difficult or even impossible with all the other methods (iron(I) + carbocation source, iron(II) + radical source, iron(III) + carbanion source) that lead to the $\text{Fe}^{\text{III}}\text{R}$ complex as the primary product. The latter complex is indeed quite unstable in the case of secondary and tertiary alkyls.

σ -Alkyl iron(III) porphyrins with secondary and tertiary alkyls decompose into the alkyl radical and the iron(II) porphyrin. The driving force for their decomposition is 0.2–0.3 eV larger than for the $\text{Fe}^{\text{II}}\text{R}^-$ oxidation state. It accelerates in the order primary < secondary < tertiary and also when going to less and less electron-rich porphyrin rings. The latter variation clearly parallels the difference in standard potentials between the $\text{Fe(II)}/\text{Fe(I)}^-$ and $\text{Fe}^{\text{III}}\text{R}/\text{Fe}^{\text{II}}\text{R}^-$ couples that measure the relative instabilities of the $\text{Fe}^{\text{III}}\text{R}$ and $\text{Fe}^{\text{II}}\text{R}^-$ complexes.

Two other oxidation states of the σ -alkyl iron porphyrins are readily obtained electrochemically from the initial $\text{Fe}^{\text{II}}\text{R}^-$ complex, namely, $\text{Fe}^{\text{I}}\text{R}^{2-}$ and $\text{Fe}^{\text{IV}}\text{R}^+$. The instability of the $\text{Fe}^{\text{I}}\text{R}^{2-}$ complex increases in the order primary < secondary < tertiary and also when going to more and more electron-rich porphyrin rings; decomposition then leads to the alkyl radical or the carbanion.

$\text{Fe}^{\text{IV}}\text{R}^+$ is quite unstable, decomposing into the alkyl radical and Fe(III) . It appears at low temperature (–50 °C) in the case of *n*-Bu and *sec*-Bu but not in the case of *t*-Bu.

Experimental Section

Chemicals. The DMF and butyl bromides, from commercial origin, were distilled before use. NEt_4ClO_4 (Fluka purum) was

used as supporting electrolyte. It was recrystallized twice before use in a 3:1 ethyl acetate–ethanol mixture. The (TPP)/ FeCl , (TPF₅P)/ FeCl , and (OEP)/ FeCl porphyrins were from commercial origin (Alfa, Aldrich) and were used as received. The (ETIO)-P/FeCl porphyrin was prepared by insertion of iron into the free base (Sigma).^{15a} The (e-(diC₃Ph)₂-CT-TPP)/ FeCl , (e-(C₁₂)₂-CT-TPP)/ FeCl , and (a-(diC₄Ph)₂-CT-TPP)/ FeCl porphyrins were provided by M. Momenteau. They were prepared and characterized as described in ref 15b,c.

Instrumentation. Instrumentation and procedures for cyclic voltammetry, thin-layer spectroelectrochemistry, and preparative scale electrolysis were the same as previously described.^{5a,6,16}

Acknowledgment. M. Momenteau (Institut Curie, Orsay) is gratefully thanked for the gift of samples of the three basket-handle porphyrins used in this work.

Registry No. (TPF₅P)Fe^{II}, 79231-62-2; (TPF₅P)(Fe^I)⁻, 120361-78-6; (TPF₅P)(Fe⁰)²⁻, 120361-80-0; (TPF₅P)Fe^{III}-*n*-Bu, 120361-83-3; (TPF₅P)Fe^{III}-*sec*-Bu, 120361-88-8; (TPF₅P)Fe^{III}-*t*-Bu, 120361-91-3; (TPF₅P)Fe^{II}-*n*-Bu⁻, 120361-96-8; (TPF₅P)Fe^{II}-*sec*-Bu⁻, 120362-02-9; (TPF₅P)Fe^{II}-*t*-Bu⁻, 120362-05-2; (TPF₅P)Fe^I-*n*-Bu²⁻, 120362-10-9; (TPF₅P)Fe^I-*sec*-Bu²⁻, 120362-17-6; (TPF₅P)Fe^I-*t*-Bu²⁻, 120362-19-8; (TPP)Fe^{II}, 16591-56-3; (TPP)(Fe^I)⁻, 54547-68-1; (TPP)(Fe⁰)²⁻, 90838-22-5; (TPP)Fe^{III}-*n*-Bu, 79198-00-8; (TPP)Fe^{III}-*sec*-Bu, 120361-89-9; (TPP)Fe^{III}-*t*-Bu, 120361-92-4; (TPP)Fe^{II}-*n*-Bu⁻, 120361-97-9; (TPP)Fe^{II}-*sec*-Bu⁻, 120362-03-0; (TPP)Fe^{II}-*t*-Bu⁻, 120362-06-3; (TPP)Fe^I-*n*-Bu²⁻, 120362-11-0; (TPP)Fe^I-*sec*-Bu²⁻, 120362-18-7; (TPP)Fe^I-*t*-Bu²⁻, 120362-20-1; (OEP)Fe^{II}, 61085-06-1; (OEP)(Fe^I)⁻, 63455-43-6; (OEP)(Fe⁰)²⁻, 105162-67-2; (OEP)Fe^{III}-*n*-Bu, 79198-01-9; (OEP)Fe^{III}-*t*-Bu, 120361-93-5; (OEP)Fe^{II}-*n*-Bu⁻, 120361-98-0; (OEP)Fe^{II}-*t*-Bu⁻, 120362-07-4; (OEP)Fe^I-*n*-Bu²⁻, 120362-12-1; (OEP)Fe^I-*t*-Bu²⁻, 120362-21-2; (ETIOP)Fe^{II}, 14566-50-8; (ETIOP)(Fe^I)⁻, 63455-36-7; (ETIOP)(Fe⁰)²⁻, 120361-81-1; (ETIOP)Fe^{III}-*n*-Bu, 120361-84-4; (ETIOP)Fe^{III}-*sec*-Bu, 120361-90-2; (ETIOP)Fe^{III}-*t*-Bu, 120361-94-6; (ETIOP)Fe^{II}-*n*-Bu⁻, 120361-99-1; (ETIOP)Fe^{II}-*sec*-Bu⁻, 120362-04-1; (ETIOP)Fe^{II}-*t*-Bu⁻, 120362-08-5; (ETIOP)Fe^I-*n*-Bu²⁻, 120362-13-2; (a-(diC₄Ph)₂-CT-TPP)Fe^{II}, 120385-08-2; (a-(diC₄Ph)₂-CT-TPP)(Fe^I)⁻, 104423-58-7; (a-(diC₄Ph)₂-CT-TPP)(Fe⁰)²⁻, 104423-59-8; (a-(diC₄Ph)₂-CT-TPP)Fe^{III}-*n*-Bu, 120361-85-5; (a-(diC₄Ph)₂-CT-TPP)Fe^{III}-*t*-Bu, 120361-95-7; (a-(diC₄Ph)₂-CT-TPP)Fe^{II}-*n*-Bu⁻, 120362-00-7; (a-(diC₄Ph)₂-CT-TPP)Fe^{II}-*t*-Bu⁻, 120362-09-6; (a-(diC₄Ph)₂-CT-TPP)Fe^I-*n*-Bu²⁻, 120362-14-3; (a-(diC₄Ph)₂-CT-TPP)Fe^I-*t*-Bu²⁻, 120362-22-3; (a-(C₁₂)₂-AC-TPP)Fe^{II}, 104423-86-1; (a-(C₁₂)₂-AC-TPP)(Fe^I)⁻, 90898-44-5; (a-(C₁₂)₂-AC-TPP)(Fe⁰)²⁻, 90898-45-6; (a-(C₁₂)₂-AC-TPP)Fe^{III}-*n*-Bu, 120443-04-1; (a-(C₁₂)₂-AC-TPP)Fe^{II}-*n*-Bu⁻, 120385-09-3; (a-(C₁₂)₂-AC-TPP)Fe^I-*n*-Bu²⁻, 120362-15-4; (a-(C₁₂)₂-CT-TPP)Fe^{II}, 93646-94-7; (a-(C₁₂)₂-CT-TPP)(Fe^I)⁻, 90838-20-3; (a-(C₁₂)₂-CT-TPP)(Fe⁰)²⁻, 90838-23-6; (a-(C₁₂)₂-CT-TPP)Fe^{III}-*n*-Bu, 120361-86-6; (a-(C₁₂)₂-CT-TPP)Fe^{II}-*n*-Bu⁻, 120410-38-0; (a-(C₁₂)₂-CT-TPP)Fe^I-*n*-Bu²⁻, 120362-16-5; (e-(diC₃Ph)₂-CT-TPP)Fe^{II}, 70196-66-6; (e-(diC₃Ph)₂-CT-TPP)(Fe^I)⁻, 120361-79-7; (e-(diC₃Ph)₂-CT-TPP)(Fe⁰)²⁻, 120361-82-2; (e-(diC₃Ph)₂-CT-TPP)Fe^{III}-*n*-Bu, 120361-87-7; (e-(diC₃Ph)₂-CT-TPP)Fe^{II}-*n*-Bu⁻, 120362-01-8; (e-(C₁₂)₂-CT-TPP)Fe^{II}, 70196-65-5; (e-(C₁₂)₂-CT-TPP)(Fe^I)⁻, 79209-91-9; (e-(C₁₂)₂-CT-TPP)(Fe⁰)²⁻, 90838-06-5; (e-(C₁₂)₂-CT-TPP)Fe^{III}-*n*-Bu, 79197-77-6; (e-(C₁₂)₂-CT-TPP)Fe^{II}-*n*-Bu⁻, 79197-78-7; *sec*-BuBr, 78-76-2; *t*-BuBr, 507-19-7; *n*-BuBr, 109-65-9; Pt, 7440-06-4; carbon, 7440-44-0.

(15) (a) Baudreau, C. A.; Caughey, W. S. *Biochemistry* 1968, 7, 624. (b) Momenteau, M.; Mispelter, J.; Look, B.; Bisagni, E. *J. Chem. Soc., Perkin Trans. 1* 1983, 189. (c) Momenteau, M.; Mispelter, J.; Look, B.; Lhoste, J. M. *J. Chem. Soc., Perkin Trans 1* 1985, 221.

(16) Lexa, D.; Savéant, J. M.; Su, K. B.; Wang, D. L. *J. Am. Chem. Soc.* 1987, 109, 6464.