# Reactions of Alkyl and Fluoroalkyl Radicals with Nickel, Iron, and Manganese Porphyrins

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The reactions of alkyl (CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, n-C<sub>4</sub>H<sub>9</sub>, CH<sub>2</sub>CO<sub>2</sub><sup>-</sup>, CH(CO<sub>2</sub><sup>-</sup>)<sub>2</sub>, CH<sub>2</sub>CN) and fluoroalkyl (CF<sub>3</sub>, CF<sub>2</sub>Cl) radicals with nickel, iron, and manganese porphyrins (P) have been studied by radiolytic techniques in various solvents. All the radicals (R) react with Fe<sup>II</sup>P to form R-Fe<sup>III</sup>P with a stable Fe-C bond. These products are oxidized by O<sub>2</sub> to Fe<sup>III</sup>P. Although Ni<sup>II</sup>P and Ni<sup>II</sup>P also react rapidly with the radicals to form Ni-C bonds, only the reactions of fluoroalkyl radicals with Ni<sup>IP</sup> yield stable products. Reactions of alkyl radicals with Ni<sup>IP</sup> result in unstable R-Ni<sup>II</sup>P products ( $t_{1/2}$  several seconds) that eventually yield Ni<sup>II</sup>P. Reactions of alkyl radicals with Ni<sup>II</sup>P are reversible, and the short-lived R-Ni<sup>III</sup>P products ( $t_{1/2} \sim$  milliseconds) disappear through radical reactions, with recovery of Ni<sup>II</sup>P. Alkyl radicals react rapidly with Mn<sup>III</sup>P, probably via addition to the metal, but the adduct gives Mn<sup>III</sup>P immediately. "CF<sub>3</sub> radicals also react with Mn<sup>III</sup>P by addition to C=-C bonds.

### Introduction

Metal-carbon bonds often play a role in the chemistry of organic compounds and metal complexes, including several of biological importance. Therefore, Fe-C and Co-C bonds in metalloporphyrins<sup>1</sup> and other related species<sup>2</sup> have been examined in detail. Ni-CH<sub>3</sub> bonding has been implicated<sup>3</sup> in the mechanism of methyl coenzyme M reductase, where factor  $F_{430}$  (nickel corphin) catalyzes the final step of methane production in bacteria. Ni-C bonds have been studied mainly with the aquo ion<sup>4</sup> and with the tetramethylcyclam complex,<sup>5</sup> and we report here on their occurrence in porphyrins. Nickel porphyrins generally are produced and stable in the oxidation state +2 (Ni<sup>II</sup>P). One-electron reduction of these metalloporphyrins may result in addition of an electron to the ligand  $\pi$ -system or to the metal. Several nickel(II) porphyrins have been shown to be reduced at the metal center to give Ni<sup>I</sup>P,<sup>6,7,8</sup> and these products were relatively unstable in aqueous solutions. If these species are produced under conditions where alkyl radicals are also formed, one may expect a reaction between the alkyl radicals and Ni<sup>I</sup>P to form Ni-C bonds, as found for other complexes of Ni<sup>I.4,5</sup>

Manganese porphyrins also have attracted attention<sup>9</sup> because of their close resemblance to the biologically important iron porphyrins and because a Mn compound is involved in the photosynthetic oxidation of water to oxygen.<sup>10</sup> A number of redox reactions involving the various oxidation states of MnP have been investigated,<sup>11</sup> but little has been reported on the metal-carbon bonds of Mn,<sup>12</sup> perhaps due to their short lifetimes. Therefore, we reacted several alkyl and substituted alkyl radicals with various oxidation states of manganese porphyrins to investigate the possible formation and stability of metal-carbon bonds and to compare them to the well-known cases of iron and cobalt porphyrins and to the recent results on CrP.<sup>13</sup>

We have utilized radiolytic techniques for the reduction of porphyrins, production of alkyl radicals, and observation of the reactions of these radicals with the reduced or nonreduced porphyrins. Spectra of transient species and their kinetics were determined by pulse radiolysis, and stable products were measured after  $\gamma$ -radiolysis, as described before for FeP<sup>14</sup> and other metalloporphyrins.<sup>15</sup> We find that both Ni<sup>1</sup>P and Ni<sup>11</sup>P react with alkyl radicals rapidly to produce Ni–C bonds but that, in most cases, these adducts are unstable. Only the fluorinated alkyl radicals gave stable products. Mn<sup>11</sup>P also reacts rapidly with alkyl radicals, but the products are only Mn<sup>111</sup>P. \*CF<sub>3</sub> radicals are found to add to the ring of Mn<sup>111</sup>P. We have also studied the parallel reactions with iron(II) porphyrins, for comparison with the other metalloporphyrins and with previous results on Fe-C bonds in metalloporphyrins.<sup>1,9,16-18</sup>

# Experimental Section<sup>19</sup>

The following abbreviations are used for the porphyrins: TPP (meso-tetraphenylporphyrin), TSPP [meso-tetrakis(4-sulfonatophenyl)porphyrin], HMP (hematoporphyrin), MSP (mesoporphyrin-IX), DP (deuteroporphyrin), and DPDME (deuteroporphyrin dimethyl ester). Iron(III), nickel(II), and manganese(III) porphyrins were obtained from Mid-Century (Posen, IL). All other reagents and solvents were of analytical grade purity and were used as received. Dimethyl sulfoxide (DMSO), iodomethane, bromoacetic acid, and succinic acid were from Aldrich. Acetonitrile, acetone, methanol, 2-propanol, toluene,  $CCl_4$ , sodium formate, and the inorganic compounds were analytical grade reagents from Mallinckrodt. *n*-Bromobutane was from Eastman. Malonic acid and *tert*-butyl alcohol were from Fisher. Water was purified with a Millipore Super-Q system.

Solutions containing  $10^{-5}-10^{-4}$  mol L<sup>-1</sup> metalloporphyrin in the desired medium were freshly prepared before use and were irradiated after purging with N<sub>2</sub>, N<sub>2</sub>O, or haloalkane gas. Steady-state irradiations were done in a Gammacell 220 <sup>60</sup>Co source with a dose rate of 1.5 Gy s<sup>-1</sup>. Pulse radiolysis experiments were performed with the apparatus described before,<sup>7</sup> which utilizes 50-ns pulses of 2-MeV electrons from a Febetron Model 705 pulser. The dose per pulse, determined by KSCN dosimetry,<sup>20</sup> was generally 13-40 Gy, which in aqueous solutions gives (8-24) × 10<sup>-6</sup> mol L<sup>-1</sup> radicals. All experiments were carried out at room temperature,  $22 \pm 2$  °C.

#### **Results and Discussion**

**Production of Radicals.** Radiolysis of aqueous solutions leads to production of several radicals:

$$H_2O \longrightarrow e_{aq}^-, H^\bullet, OH^\bullet, H^+, H_2, H_2O_2$$
 (1)

Hydrated electrons reduce metalloporphyrins (MP), but H atoms and OH radicals mostly add to the ligand. To prevent the addition reactions, it is necessary to scavenge H and OH with another solute. For example, 2-propanol reacts with H and OH rapidly to form a reducing radical,  $(CH_3)_2$ COH or its anionic form  $(CH_3)_2$ CO<sup>-</sup>  $(pK_a = 12)$ :

 $(CH_3)_2CHOH + OH^{\bullet}(H^{\bullet}) \rightarrow (CH_3)_2COH + H_2O(H_2)$  (2)

The porphyrin is reduced by reaction 3, which is known to be diffusion-controlled with many metalloporphyrins,<sup>21</sup> and by re-

action 4 with  $(CH_3)_2\dot{C}OH$  or  $(CH_3)_2\dot{C}O^-$ , with somewhat lower rate constants.<sup>22</sup>

$$MP + e_{aq}^{-} \rightarrow (MP)^{-}$$
(3)

$$MP + (CH_3)_2\dot{C}OH \rightarrow (MP)^- + (CH_3)_2CO + H^+$$
 (4)

To study the reactions of a reduced metalloporphyrin with an organic radical, it is convenient to utilize one of the above processes for reduction of the porphyrin and replace the other with a process that yields the desired radical. One possibility is to replace reaction 3 by the reductive dehalogenation reaction (5). Most alkyl halides

$$RCl + e_{ac}^{-} \rightarrow R + Cl^{-}$$
(5)

will compete with the porphyrin for the solvated electrons but will not compete with reaction 4 of the porphyrin with the  $(CH_3)_2\dot{C}OH$ or  $(CH_3)_2\dot{C}O^-$  radicals. CF<sub>3</sub>Br, on the other hand, also reacts with  $(CH_3)_2\dot{C}O^-$  at high pH.<sup>23</sup> Such reactions have been carried out in aqueous and 2-PrOH solutions, and as we show here, they also take place efficiently in toluene/acetone/2-PrOH (8:1:1) mixtures for use with porphyrins that are not soluble in water. The other possibility is to reduce the porphyrin by reaction 3 and utilize the OH radicals for production of the desired organic radical (one that does not reduce the porphyrin). This method has been applied before for production of radicals by hydrogen abstraction, e.g., from t-BuOH, acetate, malonate, acetonitrile, and is used here also for production of methyl radicals from DMSO.<sup>24</sup>

$$(CH_3)_2SO + OH^{\bullet} \rightarrow (CH_3)_2SOOH \rightarrow {}^{\bullet}CH_3 + CH_3SOOH$$
(6)

Both of these procedures give nearly equal yields of reduced porphyrin and organic radical, which then may react by reaction 7, e.g., for reduced nickel porphyrin.

$$Ni^{I}P + R^{\bullet} \rightarrow R - Ni^{II}P \tag{7}$$

**Reduction of Nickel(II) Porphyrins.** Radiolytic reduction of Ni<sup>II</sup>HMP was carried out in N<sub>2</sub>-purged aqueous solution containing 10% 2-PrOH at pH 13. The transient differential absorption spectrum in the range of 460–800 nm, monitored by pulse radiolysis immediately after the reduction reactions were complete (~100  $\mu$ s), indicates bleaching of the Q-band of Ni<sup>II</sup>P and formation of weak broad absorption at longer wavelengths. The differential spectra for reduction of Ni<sup>II</sup>DP and Ni<sup>II</sup>TSPP were similar to those reported before,<sup>7</sup> indicating that all these nickel(II) porphyrins are reduced to the Ni<sup>I</sup> state. In all cases, the Ni<sup>I</sup>P products decayed at high pH within seconds. The decay of Ni<sup>I</sup>TSPP was found to be accelerated at lower pH (half-lives of 7 ms at pH 6.8, 0.4 ms at pH 4.8, and 0.2 ms at pH 3.7).

Steady-state radiolysis of Ni<sup>II</sup>HMP under the same conditions did not show any change in the absorption spectrum up to a dose that produced reducing radicals in large excess (5 times) over the porphyrin concentration. This finding suggests that Ni<sup>I</sup>HMP is probably oxidized by the solvent. With larger doses of radiation, the peaks are gradually broadened into featureless spectra, indicating reductive decomposition of the porphyrin system. Similar results were obtained with Ni<sup>II</sup>DP and Ni<sup>II</sup>TSPP, except that in these cases long irrdiations led to formation of some nickel(II) chlorins ( $\lambda_{max}$  near 600 nm).

**Reaction of Nickel(I) Porphyrins with Methyl Radicals.** The reaction of Ni<sup>1</sup>P with methyl radicals has been studied under conditions where reduction of Ni<sup>11</sup>P and formation of methyl radicals occurred simultaneously, as described above. Pulse radiolysis experiments with deoxygenated aqueous solutions containing Ni<sup>11</sup>HMP or Ni<sup>11</sup>DP ( $10^{-4}-10^{-5}$  mol L<sup>-1</sup>) and DMSO (0.1 mol L<sup>-1</sup>) at pH 12 showed two successive reactions (Figure 1a and the adjoining traces). In the initial step ( $\sim 5 \mu$ s), the porphyrin is reduced to Ni<sup>12</sup>P (reaction 3) as is evident from the similarity of the initial differential spectrum with that found in the reduction experiment. Subsequently, a second-order reaction took place over 50  $\mu$ s to produce CH<sub>3</sub>-Ni<sup>11</sup>P (reaction 7). This product was stable over several seconds, but  $\gamma$ -radiolysis experiments indicated that it is unstable at longer times and reverts to Ni<sup>11</sup>P.  $\gamma$ -Radiolysis experiments gave the same results when



Figure 1. Reaction of methyl radicals with Ni<sup>1</sup>DP and Ni<sup>II</sup>DP. (a) Differential absorption spectra observed upon pulse radiolysis of deoxygenated aqueous solution containing 1% DMSO and  $\sim 5 \times 10^{-5}$  mol L<sup>-1</sup> Ni<sup>II</sup>DP at pH 11, monitored 5  $\mu$ s (circles) and 50  $\mu$ s (solid line) after the pulse, showing the initial reduction to Ni<sup>1</sup>DP and its subsequent reaction with methyl radicals. The adjoining traces show changes in absorbance with time at 550 (top) and 570 nm (bottom). (b) Differential absorption spectrum observed upon pulse radiolysis of N<sub>2</sub>O-saturated aqueous solution containing 1% DMSO and  $\sim 5 \times 10^{-5}$  mol L<sup>-1</sup> Ni<sup>II</sup>DP at pH 11, monitored 20  $\mu$ s after the pulse. The adjoining traces show changes in absorbance with time at 550 (top) and 570 nm (bottom).

the 2-PrOH/CH<sub>3</sub>Cl mixture (reactions 4, 5, and 7) was used instead of DMSO. In all cases, the original spectrum of the porphyrin remained unchanged after irradiation with doses that were sufficient to produce a large excess of radicals.

**Reaction of Nickel(II) Porphyrins with Methyl Radicals.** To study the reaction of methyl radicals with Ni<sup>II</sup>P, it is necessary to prevent the reduction of the porphyrin. Saturation of the solution with N<sub>2</sub>O converts the hydrated electron into OH radicals, which then reacts with DMSO to produce 'CH<sub>3</sub> radicals. Thus, these radicals can react only with Ni<sup>II</sup>P. Steady-state radiolysis experiments showed no change in the absorption of the porphyrin under these conditions. Pulse radiolysis experiments, however, indicated the presence of one process that is ascribed to reaction 8. The differential spectrum (Figure 1b), assigned to the for-

$$Ni^{II}P + CH_3^* \rightarrow CH_3Ni^{III}P$$
 (8)

mation of CH<sub>3</sub>-Ni<sup>III</sup>P, shows strong bleaching of the Q-bands (515 and 560 nm for HMP; 510 and 550 nm for DP) and similarly sharp absorptions in the same region (540 and 580 nm for HMP; 530 and 565 nm for DP). In contrast with CH<sub>3</sub>-Ni<sup>II</sup>P, the spectrum ascribed to CH<sub>3</sub>-Ni<sup>III</sup>P disappears quite rapidly ( $t_{1/2} \le 0.2$  ms for DP at pH 12). The decay is ascribed to the equilibrium reaction

$$CH_3Ni^{III}P \rightleftharpoons CH_3 + Ni^{II}P$$
 (9)

followed by

$$^{\circ}CH_3 + ^{\circ}CH_3 \text{ (or } ^{\circ}CH_3 + CH_3Ni^{III}P) \rightarrow C_2H_6$$
 (10)

as suggested before for Ni<sup>11</sup>TSPP.<sup>25</sup>

Reaction of Nickel Porphyrins with Fluoromethyl Radicals. Since the products of the reaction of methyl radicals with both Ni<sup>I</sup>P and Ni<sup>II</sup>P were found to be unstable and since the CF<sub>3</sub>-Ni bond in organo-Ni compounds is known to be more stable than the CH<sub>3</sub>-Ni bond,<sup>26</sup> we examined the reactions of °CF<sub>3</sub> and °CF<sub>2</sub>Cl radicals with both oxidation states of NiP. Aqueous solutions containing Ni<sup>II</sup>DP or Ni<sup>II</sup>HMP and 10% 2-PrOH at pH 12 were saturated with CF<sub>3</sub>Br or CF<sub>2</sub>Cl<sub>2</sub> and then irradiated.  $\gamma$ -Radiolysis results in changes in absorbance that are linearly dependent on



Figure 2. Reaction of 'CF<sub>3</sub> radicals with Ni<sup>1</sup>DP. (a) Absorbance changes observed upon  $\gamma$ -radiolysis of CF<sub>3</sub>Br-saturated aqueous solution containing 10% 2-PrOH and ~5 × 10<sup>-5</sup> mol L<sup>-1</sup> Ni<sup>III</sup>DP at pH 11. Solid line, before irradiation; dashed lines, after irradiation for 66 and 132 s. Although the process appears incomplete, further irradiation shifted the crossing points and gave different products. (b) Differential absorption spectrum observed upon pulse radiolysis of a similar solution, monitored 0.5 ms after the pulse.



Figure 3. Reaction of 'CF<sub>3</sub> radicals with Ni<sup>II</sup>DP. Differential absorption spectrum observed upon pulse radiolysis of CF<sub>3</sub>Br-saturated aqueous solution containing 10% 2-PrOH and  $\sim 5 \times 10^{-5}$  mol L<sup>-1</sup> Ni<sup>II</sup>DP at pH 13, monitored 0.1 ms after the pulse. The insert shows the time profile of the absorbance at 560 nm.

dose and show three well-defined isosbestic points at 428, 550, and 574 nm (Figure 2a). Pulse radiolysis experiments show two successive reactions. The initial step is reduction of the porphyrin within 20-30  $\mu$ s after the pulse, which gives the transient Ni<sup>1</sup>P as shown in Figures 1a. Subsequent changes in absorption appear to follow a second-order process and result in the formation of a stable product within ~1 ms. The differential spectrum for this product (Figure 2b) is identical to that calculated from the  $\gamma$ -radiolysis result. The spectra of the final products monitored by pulse and by  $\gamma$ -radiolysis with the two porphyrins reacting with the two radicals were very similar. These stable products are most probably formed by reaction of Ni<sup>1</sup>P with the fluoroalkyl radicals and contain a Ni-C  $\sigma$ -bond. They are quantitatively reoxidized by O<sub>2</sub> within several seconds to give Ni<sup>II</sup>P.

To study the reaction of  $Ni^{II}P$  with  $CF_3$  radicals, it is necessary to prevent the reduction of the porphyrin. This was done by increasing the pH to 13, where  $(CH_3)_2CO^-$  reduces  $CF_3Br$  instead of reducing the porphyrin.<sup>23</sup> Pulse radiolysis of  $Ni^{II}DP$  under these conditions indicated only one reaction, and the spectrum of the product (Figure 3) corresponds to an alkyl- $Ni^{III}$  species (based on comparison with Figure 1b). In a different experiment, pulse radiolysis of  $Ni^{II}TSPP$  was carried out in  $CF_3Br$ -saturated solutions in the absence of 2-PrOH, where both OH and  $CF_3$  radicals react with the porphyrin. The spectrum obtained under these conditions was corrected for the contribution of OH (based on



Figure 4. Reaction of *n*-butyl radicals with Fe<sup>II</sup>DP. Absorbance changes observed upon  $\gamma$ -radiolysis of deoxygenated neutral aqueous/2-PrOH (1:4) solution containing 10% *n*-C<sub>4</sub>H<sub>9</sub>Br and ~5 × 10<sup>-5</sup> mol L<sup>-1</sup> Fe<sup>III</sup>DP. Solid line, before irradiation; dashed lines, after irradiation for 66 and 132 s.

a separate experiment with N<sub>2</sub>O-saturated solution), and the corrected spectrum was similar to that of CH<sub>3</sub>-Ni<sup>III</sup>TSPP. The CF<sub>3</sub>-Ni<sup>III</sup>P species observed in the pulse radiolysis decay within 10-100 ms, probably via an equilibrium similar to reaction 9. They are somewhat longer lived than CH<sub>3</sub>-Ni<sup>III</sup>P but are not sufficiently stable, as is CF<sub>3</sub>-Ni<sup>II</sup>P, to be observed following  $\gamma$ -radiolysis.

**Reaction of Alkyl and Fluoroalkyl Radicals with Iron Porphyrins.** In contrast with the short lifetime of alkyl-NiP discussed above, alkyl-Fe<sup>III</sup>P are generally stable under anaerobic conditions. Nevertheless, differences in behavior have been noted between the fluorinated and non-fluorinated alkyl and aryl derivatives. Radiolytic reduction of Fe<sup>III</sup>P to Fe<sup>II</sup>P and the reactions of the latter with 'CH<sub>3</sub> and 'CF<sub>3</sub> radicals, leading to formation of Fe-C bonds, have been studied before.<sup>14,16</sup> Whereas CH<sub>3</sub>-Fe<sup>III</sup>DP was relatively resistant to further reduction, CF<sub>3</sub>-Fe<sup>III</sup>DP was found to be reduced by Fe<sup>II</sup>DP and undergoes defluorination and hydrolysis to CO-Fe<sup>II</sup>DP.<sup>16</sup> In contrast, fluoroaryl-Fe<sup>III</sup>P has been reported to be reduced to fluoroaryl-Fe<sup>II</sup>P.<sup>17</sup>

Radiolytic reduction of  $Fe^{III}DP$  ( $\lambda_{max}$  390, 470, 576 nm) in aqueous 2-PrOH solutions and of  $Fe^{III}DPDME$  in neat 2-PrOH gave the Fe<sup>II</sup>P form ( $\lambda_{max}$  408, 528, 550 nm) quantitatively, in agreement with previous results.<sup>14</sup>  $\gamma$ -Irradiation of Fe<sup>III</sup>DP in a deoxygenated neutral 2-PrOH/water (8:2) solution containing 0.1-1 mol L<sup>-1</sup> haloalkane results in spectral changes (as in Figure 4) that are clearly different from those seen upon reduction of Fe<sup>III</sup>DP and are ascribed to the formation of alkyl-Fe<sup>III</sup>P as before.<sup>14b</sup> The absorption maxima varied only slightly with the alkyl group; for CH<sub>3</sub>, 396, 520, 546 nm; for  $C_2H_5$  and  $n-C_4H_9$ , 388, 516, 546 nm; for  $CH_2CO_2^-$ , 388, 514, 546 nm; and for  $CF_3$  and  $CF_2Cl$ , 396, 522, 546 nm. These products are stable under anaerobic conditions but are oxidized within a few seconds under air to give back the starting material, Fe<sup>III</sup>DP. In the case of R = CF<sub>3</sub> and CF<sub>2</sub>Cl, further irradiation of the  $R-Fe^{III}P$  products resulted in a gradual disappearance of their spectra and appearance of two new minor bands at 428 and 598 nm. This process, occurring in neutral solution, has not been investigated further, but it has been shown before that in alkaline solutions CF<sub>3</sub>-Fe<sup>III</sup>DP can be reduced and hydrolyzed to CO-Fe<sup>II</sup>DP.<sup>16</sup>

Somewhat similar results were obtained with Fe<sup>III</sup>DPDME in nonaqueous solvents, neat 2-PrOH, and toluene/acetone/2-PrOH (8:1:1). In the former solvent, this porphyrin contains an alkoxide axial ligand, but in the latter solvent, it was mainly in the  $\mu$ -oxo dimer form. Irradiation of haloalkanes (RX) in these solvents produces acid (HX), which converts the above forms of the porphyrin into the monomeric conjugate acid (axial RO<sup>-</sup>  $\rightarrow$  ROH) form, [(ROH)<sub>2</sub>Fe<sup>III</sup>DPDME]<sup>+</sup>, with peaks at 390, 500, 530, and 630 nm.<sup>27</sup> Reaction of alkyl radicals with the reduced porphyrin gave alkyl-Fe<sup>III</sup>P, whose peaks were only slightly shifted as compared with those observed in neutral aqueous solutions.

Reaction of Alkyl and Fluoroalkyl Radicals with Manganese Porphyrins. The reactions of various alkyl radicals with  $Mn^{II}P$ and  $Mn^{III}P$  have been studied by steady-state and pulse radiolysis. Substituted alkyl radicals with reducing properties (such as  $\dot{C}H_2OH$ ,  $(CH_3)_2\dot{C}OH$ ,  $\dot{C}O_2^{-}$ ) are known to reduce  $Mn^{II}P$  to  $Mn^{II}P$ .<sup>11c</sup> These radicals were also found to reduce  $Mn^{II}P$  to the

 $\pi$ -radical anion. Nonreducing alkyl radicals, however, exhibit very low reactivity toward Mn<sup>III</sup>P but are found to react with Mn<sup>II</sup>P rapidly and to oxidize it to the Mn<sup>III</sup>P state. The latter reaction has been demonstrated for methyl radicals and for the radicals derived by H abstraction from t-BuOH, acetate, malonate, succinate, and acetonitrile. The rate constants were measured to be  $9.7 \times 10^8$  for R = CH<sub>3</sub> at pH 8.8, ~9.5 × 10<sup>8</sup> for R = °CH<sub>2</sub>C- $(CH_3)_2OH$  at pH 8.8, and 5.8 × 10<sup>8</sup> L mol<sup>-1</sup> s<sup>-1</sup> for R = •CH-(CO<sub>2</sub><sup>-</sup>)<sub>2</sub> at pH 6.6. For these experiments, Mn<sup>II</sup>TSPP was prepared by dithionite reduction of  $Mn^{III}TSPP$  in N<sub>2</sub>O-saturated solution containing the respective OH scavenger and then irradiated. The differential spectra recorded by pulse radiolysis 0.2-0.5 ms after the pulse were in agreement with those calculated from the spectra of Mn<sup>II</sup>P and Mn<sup>III</sup>P recorded before and after  $\gamma$ -radiolysis. Thus, no evidence is found for an alkyl-Mn<sup>III</sup>P species with a lifetime longer than  $\sim 0.1$  ms. Since Mn<sup>II</sup>P is oxidized by these alkyl radicals to Mn<sup>III</sup>P and since such alkyl radicals do not oxidize by an outer-sphere mechanism, it may be concluded that the oxidation takes place via a transient alkyl-Mn adduct.

$$\mathbf{R}^{\bullet} + \mathbf{Mn}^{II}\mathbf{P} \rightarrow \mathbf{R} - \mathbf{Mn}^{III}\mathbf{P} \xrightarrow{\mathbf{u}^{\bullet}} \mathbf{RH} + \mathbf{Mn}^{III}\mathbf{P}$$
(11)

The reaction of methyl radicals with Mn<sup>II</sup>MSP gave similar results.

Fluorinated alkyl radicals are generally more reactive than alkyls and are known to form more stable metal-carbon bonds. Therefore, we have examined their reactions with  $Mn^{II}P$  and  $Mn^{III}P$ .  $\gamma$ -Radiolysis of  $Mn^{III}TSPP$  in an aqueous solution containing 1% 2-PrOH and saturated with CF<sub>3</sub>Br at pH 6.8 and 9.0 resulted in reduction to  $Mn^{II}TSPP$ . Similar results were obtained with 50% and 100% 2-PrOH as solvent. Under these conditions,  $Mn^{III}TSPP$  is reduced by (CH<sub>3</sub>)<sub>2</sub>COH, as in reaction 4, and CF<sub>3</sub>Br is reduced by the solvated electrons, as in reaction 5, to give CF<sub>3</sub> radicals. These apparently react with 2-PrOH ( $k = 9 \times 10^4$  L mol<sup>-1</sup> s<sup>-1</sup>)<sup>28</sup> rather than with the porphyrin,

$$CF_3 + (CH_3)_2CHOH \rightarrow (CH_3)_2COH + CF_3H$$
 (12)

and the net result is reduction of the porphyrin. On the other hand, at pH  $\geq$  11.4, no Mn<sup>II</sup>TSPP was formed. Instead, a stable product (P<sub>1</sub>) with two broad peaks at ~570 and ~615 nm and a split Soret band similar to that of Mn<sup>III</sup>TSPP was found. The broad peaks shifted gradually on further irradiation, and no clear isosbestic points were seen (Figure 5a). Under these conditions, the (CH<sub>3</sub>)<sub>2</sub>COH radical deprotonates (pK<sub>a</sub> = 12) to give (CH<sub>3</sub>)<sub>2</sub>CO<sup>-</sup>, which then reduces CF<sub>3</sub>Br,<sup>23</sup> with  $k \sim 3 \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup>.

$$(CH_3)_2\dot{C}O^- + CF_3Br \rightarrow CF_3 + Br^- + (CH_3)_2CO$$
 (13)

Reduction of  $Mn^{III}TSPP$  will be less favorable than reaction 13 because of the much lower concentration of  $Mn^{III}TSPP$  (~4 × 10<sup>-5</sup> mol L<sup>-1</sup>). The products observed are thus due to reaction of °CF<sub>3</sub> with  $Mn^{III}TSPP$ .

$$\cdot \mathbf{CF}_3 + \mathbf{Mn}^{\mathrm{III}} \mathbf{P} \to \mathbf{P}_1 \tag{14}$$

Replacing 2-PrOH with t-BuOH or DMSO as the 'OH scavenger in the above experiment with CF<sub>3</sub>Br gave the same product on  $\gamma$ -radiolysis. Replacing CF<sub>3</sub>Br with N<sub>2</sub>O, however, resulted in little change in absorption upon  $\gamma$ -radiolysis, indicating that neither 'CH<sub>3</sub> nor 'CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>OH reacts with Mn<sup>III</sup>TSPP to give P<sub>1</sub>. Replacing CF<sub>3</sub>Br with CF<sub>2</sub>Cl<sub>2</sub> gave a similar broad spectrum, without production of any Mn<sup>II</sup>P. Replacing CF<sub>3</sub>Br with CH<sub>3</sub>Cl led to reduction of Mn<sup>III</sup>P to Mn<sup>II</sup>P and further to chlorin, since (CH<sub>3</sub>)<sub>2</sub>CO<sup>-</sup> does not react with CH<sub>3</sub>Cl. Reaction of 'CF<sub>3</sub> with Mn<sup>III</sup>MSP gave a product similar to P<sub>1</sub>.

 $P_1$  can be further reduced with  $(CH_3)_2COH$  to a product with spectral characteristics similar to those of  $Mn^{II}TSPP$ , and this reduced species can be oxidized by  $O_2$  back to the original product  $P_1$ . Furthermore, if radiolytic reduction of  $P_1$  is carried out in acid solution,  $pH \leq 2$ , the reduced  $Mn^{II}$  species demetalates to give a free base porphyrin which has a pH-dependent spectrum (Figure 5b). This free base porphyrin was separated from the  $Mn^{2+}$  ions by a cation-exchange column and then extracted with



Figure 5. Reaction of  ${}^{\circ}\text{CF}_3$  radicals with  $Mn^{III}\text{TSPP}$ . (a) Spectral changes upon  $\gamma$ -radiolysis of  $5 \times 10^{-5}$  mol L<sup>-1</sup>  $Mn^{III}\text{TSPP}$  in CF<sub>3</sub>Br-saturated aqueous solution containing 1% 2-PrOH at pH 11.4 (total irradiation time 18 min). (b) Absorption spectra of the free base obtained by reduction and demetalation of P<sub>1</sub> (from a) at pH 2.1 (solid line) and pH 10.6 (dashed line). The dotted line is the spectrum of H<sub>4</sub>TSPP<sup>2+</sup> at pH 2.2 (different concentration). (c) Differential absorption spectrum monitored by pulse radiolysis (0.6 ms after the pulse) following reaction of  ${}^{\circ}\text{CF}_3$  radicals with  $Mn^{III}\text{TSPP}$ ; solution as in a.

methanol and dried. Its elemental analysis showed the presence of an average of 3.6 F atoms per molecule (i.e., per 4 N atoms). This is compatible with the presence of mostly one CF<sub>3</sub> group per molecule of P<sub>1</sub>, with some molecules containing more than one CF<sub>3</sub> group. These results indicate that the <sup>•</sup>CF<sub>3</sub> radicals react with Mn<sup>III</sup>P by addition to the ring to result in CF<sub>3</sub>-substituted products.

The spectrum of the transient formed by the reaction of  ${}^{\circ}\text{CF}_3$ radicals with  $Mn^{III}$ TSPP was monitored by pulse radiolysis (Figure 5c). The rate constant for this reaction was found to be 9.2 ×  $10^7 \text{ L} \text{ mol}^{-1} \text{ s}^{-1}$ , as determined by following the kinetics at 530 and 590 nm at different concentrations of  $Mn^{III}$ TSPP. This rate constant in only slightly higher than those reported for addition of  ${}^{\circ}\text{CF}_3$  radicals to simple alkenes<sup>28</sup> and thus is reasonable for addition of these radicals to the double bonds of the porphyrin ring. The final product  $P_1$  is formed by disproportionation of the intermediate adducts or by their reaction with another  ${}^{\circ}\text{CF}_3$  and thus may be a mixture of substituted chlorins and porphyrins.

In summary, the reactions of alkyl and fluoroalkyl radicals with Mn<sup>II</sup>P lead to its oxidation to Mn<sup>III</sup>P but not to stable R-Mn<sup>III</sup>P, although the adducts may be formed as short-lived intermediates. This is a result of the high-spin d<sup>5</sup> configuration of Mn<sup>II</sup>, which

also causes it to be displaced from the porphyrin plane and to have weak Mn-N bonds, thus demetalating readily.

Comparison of the Different Metalloporphyrins. Numerous studies have described stable metal-carbon  $\sigma$ -bond formation in Fe and Co complexes with porphyrins and other ligands. The present results on iron porphyrin reactions with alkyl and fluoroalkyl radicals, producing stable R-Fe<sup>III</sup>P complexes, are consistent with previous observations. CF<sub>3</sub>-Fe<sup>III</sup>P has been reported to undergo reductive defluorination and hydrolysis in aqueous alkaline solutions to yield CO-Fe<sup>II</sup>P. CF<sub>3</sub>-Co<sup>III</sup>(cobamides) also have been reported to undergo reductive defluorination in aqueous solution, but the product in this case was identified as CF<sub>2</sub>H-Co<sup>III</sup>(cobamide).<sup>29</sup> The mechanism was suggested to involve reductive defluorination, followed by a second reduction to a carbene and finally protonation. Possibly, the difference between this mechanism and that found with CF<sub>3</sub>-Fe<sup>III</sup>P is due to the pH difference; the latter has been studied in alkaline solution, where hydrolysis of the difluorocarbene group into CO is more feasible than protonation.

In contrast with the demonstrated stability of R-Fe<sup>III</sup>P and R-Co<sup>III</sup>P. R-Ni<sup>II</sup>P and R-Ni<sup>III</sup>P are generally short-lived. Such species were suggested to exist as short-lived intermediates in the reaction of nickel(I) isobacteriochlorin with CH<sub>3</sub>I.<sup>30</sup> In the present study, they were produced by reaction of alkyl radicals with Ni<sup>I</sup>P and Ni<sup>II</sup>P and were observed as transients in the pulse radiolysis experiments. Most of them decay through reactions of the alkyl radical existing in equilibrium with the complex. Only CF<sub>3</sub>-Ni<sup>II</sup>P was sufficiently long-lived to be observed following production by  $\gamma$ -radiolysis. This increased stability of the CF<sub>1</sub>-Ni complex as compared with the CH<sub>3</sub>-Ni analogue is in-line with previous observations on organo-Ni compounds.<sup>26</sup> The effect is ascribed to the higher electron affinity of the CF<sub>3</sub> group which stabilizes the adduct by lowering the electron density on the Ni (producing more Ni<sup>II</sup> character) and thus decreasing its ionic radius.

The large ionic radius of Ni<sup>I</sup> has been implicated in causing the instability of nickel(I) porphyrins and other nickel(I) macrocyclic complexes. Stable Nil complexes have been observed with isobacteriochlorin (iBC) and factor  $F_{430}$ .<sup>31</sup> These monovalent Ni complexes have been shown to contain two different sets of Ni-N bonds (iBC, 1.85 and 2.00 Å; factor  $F_{430}$ , 1.88 and 2.03 Å), while in their divalent state all four Ni-N bonds were equidistant (iBC, 1.93 Å; factor  $F_{430}$ , 1.90 Å). This finding has been ascribed to the flexibility of these macrocycles, which, in their ruffled structure, can accommodate the large Ni<sup>I</sup> ion (0.95 Å).<sup>32</sup> On the other hand, the more restricted geometry of the rigid porphyrin and its relatively small size (in Ni<sup>II</sup>P, the Ni-N bond length is 1.93-1.96 Å)<sup>33</sup> prevents stabilization of the Ni<sup>I</sup> complex. Nickel porphyrins form a square-planar complex as demonstrated for a large number of complexes with d<sup>8</sup> and d<sup>9</sup> ions. In these cases, the d orbitals are split into four levels. The lack of axial ligands in square-planar complexes causes the  $d_{r^2}$  orbital to be at a lowenergy level. In nickel porphyrins (d<sup>8</sup> Ni<sup>II</sup> or d<sup>9</sup> Ni<sup>I</sup>), this orbital is doubly-occupied, and thus attack by an alkyl radical cannot lead to a stable Ni-C bond. The even larger ionic radius of Cu<sup>I</sup>  $(0.96 \text{ Å})^{34}$  causes Cu<sup>II</sup>P to be reduced on the ligand to form the  $\pi$ -radical anion.

Chromium porphyrins have been shown to be reduced to stable Cr<sup>II</sup>P under certain conditions, and moreover, stable alkyl adducts have been produced with both Cr<sup>II</sup>P and Cr<sup>III</sup>P.<sup>13</sup> Alkylation of these complexes resulted in a decrease in the rate of their air oxidation. While Cr<sup>II</sup>P undergoes air oxidation within seconds to Cr<sup>III</sup>P, various R-Cr<sup>III</sup>P exhibit lifetimes of 30-60 min. The finding of stable Cr<sup>II</sup>P can be ascribed to the moderate ionic radius of  $Cr^{II}$  (0.84 Å). This radius is considerably smaller than those of Ni<sup>1</sup> and Cu<sup>1</sup> but somewhat larger than the ionic radii of Fe<sup>11</sup> (0.76 Å) and Co<sup>II</sup> (0.74 Å), which, like Cu<sup>II</sup> (0.72 Å) and Ni<sup>II</sup> (0.72 Å), form stable porphyrin complexes. Indeed, the metal center in Cr<sup>II</sup>TPP was found to be located within the plane of the porphyrin ligand.<sup>35</sup> The energy levels of d orbitals for Cr<sup>III</sup>P under octahedral trans configuration ( $C_{4v}$  coordination) are such that the lowest unoccupied level is most likely the  $d_{z^2}$  orbital. Therefore, reduction to form a high-spin Cr<sup>II</sup>P probably leads to addition of the electron into this orbital. The singly occupied  $d_{r^2}$  orbital represents an excellent target for an alkyl radical to add an electron. These two electrons can be stabilized by interaction of the latter orbital with the  $d_{x^2-y^2}$  orbital.

Manganese(III) porphyrins have been shown to be reduced exclusively at the metal center. The relatively small size of Mn<sup>II</sup> (0.80 Å) permits its accommodation within the porphyrin ligand. However, because of its high-spin d<sup>5</sup> configuration, Mn<sup>II</sup> was found to be located outside the porphyrin plane (to lower the energy of the  $d_{x^2-y^2}$  orbital). A reaction with an alkyl radical along the z axis is expected to lead to a double occupancy of the d. orbital. Hence, this orbital would be the only one containing an electron pair. The high energy of this orbital and the fact that the three singly occupied t<sub>2g</sub> orbitals have a lower energy lead to the conclusion that the R-Mn<sup>III</sup>P state has to be highly unstable. Indeed, as indicated by the above findings, such a species is only a transient which undergoes rapid oxidation to Mn<sup>III</sup>P.

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# COMMENTS

# Generation of Metallocarbohedrene Clusters from **Titanium and Graphite Powders**

Sir: Recently, a new type of metal-carbon cluster compound was discovered during the course of studying reactions in a plasma reactor of early transition metals with various small hydrocarbons.<sup>1,2</sup> The  $M_8C_{12}$  (M = Ti, V, Zr, and Hf) cluster was observed to be both a stable cation produced in the plasma and a stable and abundant neutral reaction product, among the series of  $M_m C_n$  species. A dodecahedral structure of  $T_h$  point group symmetry was proposed to account for the unusual prominence of this new class of molecular clusters, called metallocarbohedrenes (Met-Cars). These clusters were generated employing a laser vaporization source-plasma reactor whereupon a powerful laser was focused onto the surface of the selected metal reactant over which He (the carrier gas of the supersonic expansion) containing the desired hydrocarbon (e.g., C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, and C<sub>6</sub>H<sub>6</sub>) reactant was passed.

Following the discovery of Met-Cars, experiments were conducted to gain insight into the mechanisms leading to the formation of these stable species.<sup>3</sup> The lack of any hydrogen component in the observed mass spectra of the  $M_m C_n^+$  suggested that efficient dehydrogenation reactions take place in the plasma. This raised the likelihood that either the hydrocarbons are cracked and lose their hydrogen atoms in multiple collisions with energetic electrons or other plasma constituents, or they are efficiently dehydrogenated by reactions with the transition-metal atoms or ions present in the plasma. These first studies of the reaction mechanisms raised questions about the possible role of partially dehydrogenated hydrocarbons as intermediates in the formation of Met-Cars. Also, the design of a synthesis routine for producing bulk amounts of metallocarbohedrenes depends on knowledge of the mechanisms and knowing what form of carbon should be introduced into the reactor. These have prompted us to attempt the synthesis of the Met-Cars using only metal and carbon as reactants, which is the subject of this Comment.

The details of the photoionization time-of-flight apparatus will be described in detail elsewhere,<sup>4,5</sup> and only those parts of the apparatus that relate to the results reported herein are briefly described. A modified laser vaporization source<sup>6-9</sup> is used to generate the clusters. The frequency-doubled (532 nm) output of a Nd:YAG laser (Spectra-Physics DCR-1) is focused onto the surface of a titanium and carbon-containing rod with a typical power of 10 mJ/pulse at 10 Hz. The high-temperature plasma, which contains ionic and neutral Ti, C, and Ti-carbon clusters, is carried in a supersonic gas jet produced by pulsing high-pressure He (ca. 6 atm) over the rod. The clusters are cooled in a supersonic expansion effected into vacuum through a conical-shape nozzle. After passing through a skimmer, the neutral clusters are photoionized by the frequency-tripled output (355 nm) of a second Nd:YAG laser (Spectra-Physics GCR-3) utilizing a typical fluence of 10 mJ/cm<sup>2</sup>. (We have previously ascertained that fragmen-



Figure 1. TOF mass spectrum of  $Ti_m C_n^+$  clusters prepared in a laser vaporization source using a Ti/C rod as the source for Ti and C atoms and ions in the laser-generated plasma. Ionization of the neutral clusters is accomplished by photoionization with the third harmonic of a Nd:YAG laser (355 nm, 10 mJ/cm<sup>2</sup>). Ti<sub>m</sub>C<sub>n</sub><sup>+</sup> clusters are marked as (m,n) in the spectrum. Note that  $Ti_8C_{12}^+$  appears as an abundant peak (magic) in the mass spectrum. This result shows that the  $Ti_8C_{12}$  cage is produced by direct reaction of titanium atoms with carbon atoms.

tation of these strongly bound clusters is negligible under these conditions.<sup>3</sup>) Mass analysis is accomplished with a TOF mass spectrometer; the ions are detected with a multichannel plate detector, and the signal is collected, averaged in a digital storage oscilloscope (LeCroy 9400A), and analyzed using a PC. The titanium/carbon rods were prepared from titanium powder (325 mesh, Johnson Matthey, 99% purity) along with graphite powder (particle size  $1-2 \mu m$ , with purity >99%, Aldrich Chemical Co., Inc.) in an approximate 3:1 (Ti/C) molar ratio. The powders were mixed, homogenized, and pressed in a stainless steel mold at pressures of about 6000 bar, resulting in rigid 6-mm-diameter rods.

The relative abundance of  $Ti_m C_n^+$  clusters obtained in this series of measurements is seen from typical data plotted in Figure 1. Although no hydrocarbons are present in the reactants or products in these new experiments (we paid careful attention to the possible presence of any hydrocarbon species in the low mass range of the mass spectra), the mass spectrum reveals the same product pattern as the mass spectra reported in refs 1-3, where the earlier case hydrocarbons were the carbon-containing reactant. Most notably, Ti<sub>8</sub>C<sub>12</sub><sup>+</sup> again appears as a "magic peak", providing further evidence of the special stability of this molecule. Moreover, similar to earlier results,<sup>3</sup> the magic abundance of  $Ti_8C_{12}^+$  is independent of the fluence of the ionizing laser over the ranges accessible using our apparatus.

From these findings it can be concluded that the Ti-carbon clusters, and most notably the  $Ti_8C_{12}^+$  cage, are a result of the