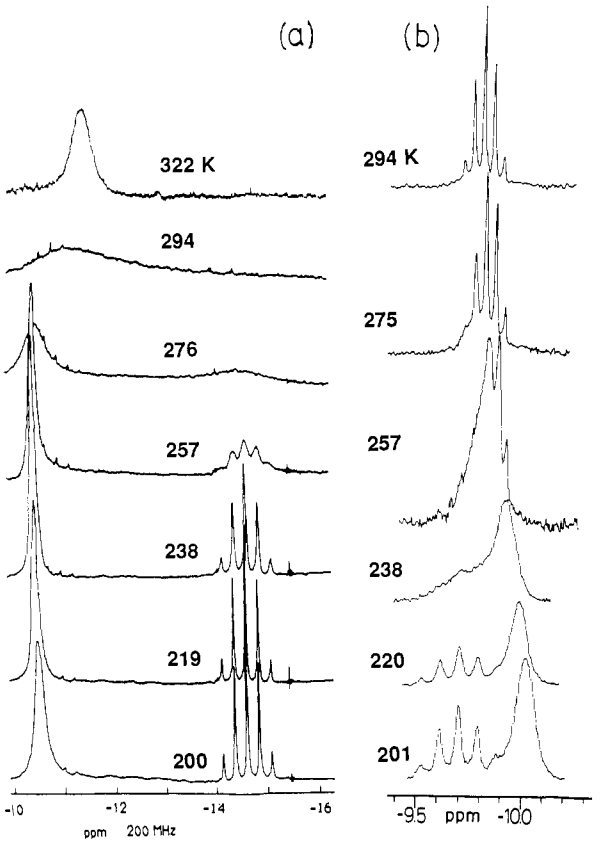

Figure 1. ^1H NMR spectra at 200 MHz as a function of temperature for the complexes **2Fe** (a) and **2Os** (b).

an attractive explanation for the hydrogen exchange process and the ordering of $\Delta G^{\ddagger}$ values for complexes **1** and **2**. However, a process involving isomerization of the octahedral complexes to bring exchanging groups cis to each other as in the complexes $[Ir(H_2)(H)(C_{13}H_8N)(PR_3)_2]^+$[5a] cannot be ruled out considering that the rate of exchange is sensitive to the nature of the phosphine ligand.

The trends in the barriers to intramolecular exchange of hydrogens, in the susceptibilities to H_2 loss, in the T_1 values, and in the couplings $^1J(H,D)$ and $^2J(\eta^2\text{-}H_2,P)$ all indicate that H–H interactions decrease in the order **1Ru > 2Ru > 1Fe > 2Fe > 2Os**. The M–H_2 interactions increase as the H–H interactions decrease. A combination of two factors could explain these trends. First, there is a general increase in metal–ligand bond strength down the group. Second, there is an increase in $d\pi \rightarrow \sigma^*$ back-donation in the order Ru < Os < Fe, dppe < depe as judged by $\nu(N_2)$ frequencies of corresponding dinitrogen complexes $[M(N_2)(H)(depe)_2]^+$[15] and $[Fe(N_2)H(dppe)_2]^+$.[23]

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Supplementary Material Available: Spectral and analytical data, table of activation parameters and rates, and figures of observed and simulated ^1H NMR spectra for complexes **1Fe**, **2Fe**, **2Os**, and HD_2 isotopomers of **2Os** (7 pages). Ordering information is given on any current masthead page.

(23) $[Fe(N_2)H(dppe)_2]BF_4$, $\nu(N_2) = 2120\ cm^{-1}$. Azizian, H.; Morris, R. H. *Inorg. Chem.* **1983**, *22*, 6–9.

Suicidal Inactivation of Iron Porphyrin Catalysts during Alk-1-ene Oxidation: Isolation of a New Type of *N*-Alkylporphyrins

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Presently, two model systems using an iron porphyrin catalyst and an iodosylarene as oxidant have been reported to mimic the suicidal inactivation of cytochrome P-450 with formation of *N*-alkylporphyrins[1] during oxidation of terminal alkenes.[2,3] Upon oxidation of alk-1-enes by the Fe(TDCPP)(Cl)[4]–C_6F_5IO system,[2] the *N*-alkylporphyrins isolated after acidic treatment had a *N*-CH_2CHOHR structure identical with that issued from experiments in vivo[1] (A_2 in Scheme I). *N*-alkylporphyrins were also formed upon oxidation of the alkenes reported to give green pigments in vivo, by the Fe(TPP or TpClPP)(Cl)[4]–PhIO system.[3]

This paper reports the isolation and structure determination of the *N*-alkylporphyrins formed by the latter system and shows that they derive from the binding of a pyrrole nitrogen to the more substituted carbon of the $RCH{=}CH_2$ alkene and not to the less substituted carbon as in the case of cytochrome P-450[1] or in the former model system.[2]

Upon reaction of but-1-ene in CH_2Cl_2 with Fe(TpClPP)(Cl)[4] (10 mM) and PhIO (35 equiv) at −10 °C, the starting catalyst was progressively transformed into a new complex **1** exhibiting a Soret peak at 447 nm and not well-defined bands around 570 and 674 nm.[3] After acidic demetalation,[3] a green porphyrin **2** exhibiting a UV–visible spectrum typical of *N*-alkylporphyrins[3] was obtained (60% yield based on the starting catalyst). Despite its great instability (as complex **1**), **2** could be studied by mass and ^1H NMR spectroscopy. From its mass spectrum (field desorption), which exhibits a molecular peak at *m/e* 838 corresponding to $TpClPPH_2 + C_4H_6O_2$ and two fragments at *m/e* 794 ($M - CO_2$) and 752 ($TpClPPH_2$), and its ^1H NMR spectrum,[5] which exhibits four signals for this chain at δ −1.2 (3 H), −2.13 (1 H), −2.66 (1 H), and −3.93 (1 H), the most probable structure for the *N*-alkyl chain was $N\text{-}CH(COOH)CH_2CH_3$. The latter structure was established by two sets of experiments. First, treatment of **2** by $CF_3SO_3CH_3$ in C_6H_6 led to the corresponding methyl ester **3**, the structure of which was definitely proved by comparison of its ^1H NMR and mass spectrum characteristics[6] with those of an authentic sample prepared by reaction of the diazo ester $N_2C(COOCH_3)C_2H_5$ with Zn(TpClPP) and demetalation of the obtained Zn–*N*-alkylporphyrin, according to a procedure described previously for other $N\text{-}CH(COOCH_3)R$ porphyrins[7]

(1) (a) Ortiz de Montellano, P. R. *Annu. Rep. Med. Chem.* **1984**, *19*, 201–211. (b) Ortiz de Montellano, P. R.; Kunze, K. L.; Beilan, H. S.; Wheeler, C. *Biochemistry* **1982**, *21*, 1331–1339.

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(4) TDCPP, TPP, and TpClPP are respectively used for the dianion of *meso*-tetrakis(2,6-dichlorophenyl)-, *meso*-tetraphenyl-, and *meso*-tetrakis(parachlorophenyl)porphyrin.

(5) ^1H NMR of **2** ($Me_2SO\text{-}d_6$): *N*-alkyl chain $N\text{-}CH_c(COOH)\text{-}CH_aH_bCH_3$, H_c (−3.93), H_b (−2.66), H_a (−2.13) assigned thanks to double irradiation and 2D NMR (COSY 90) experiments. Porphyrin signals: pyrrole H, 8.93 (2 H, s), 8.74 and 8.49 (2 H), 8.6 and 8.56 (2 H), 7.57 and 7.49 (2 H) (3 AB systems, J = 4 Hz); ortho H, 8.15–8.42 (8 H, m); meta H, 8.08 (4 H, d, J = 8.5 Hz), 7.98 (4 H, d, J = 8.5 Hz).

(6) **3**: $N\text{-}[CH_c(COOCH_3)CH_aH_bCH_3]TpClPPH$; mass spectrum, *m/e* 853 (100, MH^+), 753 (92, $TpClPPH_2$ + **1**); ^1H NMR ($Me_2SO\text{-}d_6$) 1.97 (OCH_3,s), −1.21 (3 H, t, 7.5), −1.78 (H_a, m, $J_{H_aH_b}$ = 15 Hz), −2.36 (H_b, m), −3.96 (H_c, dd, $J_{H_cH_a}$ = 8, $J_{H_cH_b}$ = 3.5); meta H 7.96 (4 H, d, J = 8 Hz), 8.04 (4 H, d, J = 8 Hz); ortho H, 8.11–8.40 (8 H); pyrrole H: 8.93 (2 H, s), 8.72 and 8.5 (2 H), 8.62 and 8.57 (2 H), 7.64 and 7.54 (2 H) (3 AB systems, J = 4.5 Hz).

(7) Callot, H. J.; Schaeffer, E. *Nouv. J. Chim.* **1980**, *4*, 307–309.

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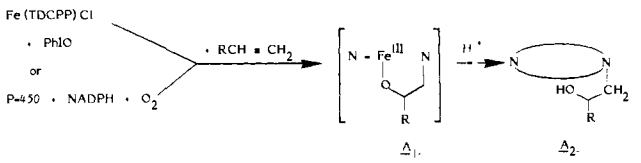
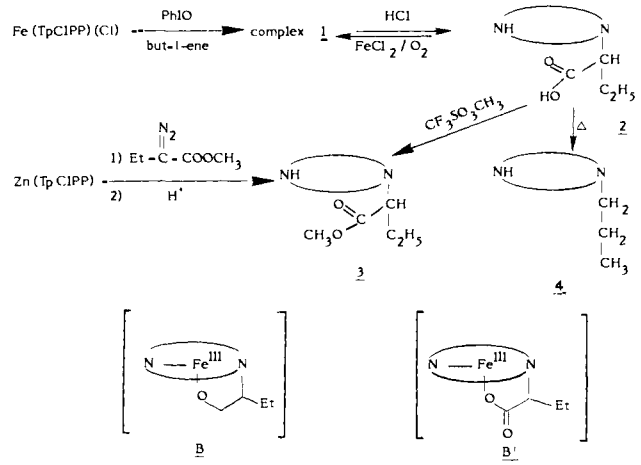
Scheme I



Scheme II



(Scheme II). Second, the simple heating of **2** in CH_3OH containing HCl for 1 h at 50 °C led to its decarboxylation. The structure of the *N*-propyl-TpClPPH, **4**, was clearly shown by its ^1H NMR and mass spectra.[8] The easy decarboxylation of **2**[9] could explain at least in part its instability.

Metalation of **2** by $FeCl_2$ in aerated THF gave an unstable complex exhibiting a UV–visible spectrum superimposable on that of complex **1**. Moreover, the analogy of this spectrum with those of previously reported iron(III) porphyrins involving a five-membered NCCOFe metallocycle[2,10] suggests the NCHEt-COOFe structure proposed for this complex (structure B′ of Scheme II).

Preliminary ^1H NMR and mass spectroscopy studies on the *N*-alkylporphyrins formed during oxidation of 4-methylpent-1-ene and hex-1-ene by PhIO catalyzed by Fe(TPP)(Cl) or Fe(TpClPP)(Cl)[4] indicated a N–CH(COOH)R porphyrin structure as in **2**. Thus, it appears that two kinds of *N*-alkylporphyrins can be isolated from 1-alkene oxidation by PhIO catalyzed by iron porphyrins: the N–CH_2CHROH porphyrins found upon oxidation of several 1-alkenes (3-methylbut-1-ene, 4,4-dimethylpent-1-ene, and dec-1-ene) by Fe(TDCPP)Cl[2] and the N–CHRCOOH porphyrins found upon oxidation of various alkenes (but-1-ene, hex-1-ene, and 4-methylpent-1-ene) by Fe(TPP or TpClPP)Cl (this work). Much work is still needed to determine the mechanism of formation of these N–CHRCOOH porphyrins. However, it is likely that complex **1** has the structure B′ indicated in Scheme II. It could be formed by oxidation in the medium containing PhIO, from a precursor B (a regioisomer of A_1 with R = Et), deriving formally from an addition of a pyrrole nitrogen to the internal carbon and the iron-activated oxygen[11] to the terminal carbon of the alkene double bond.

The above results show for the first time that *N*-alkylporphyrins deriving from the binding of a pyrrole nitrogen to the more substituted vinylic carbon of alkenes are formed during oxidation of these substrates by PhIO catalyzed by certain iron porphyrins. They suggest that the structure of the final *N*-alkylporphyrins formed in such reactions is critically dependent on the nature of the iron environment in the catalyst and on the fate of the intermediate complexes in the highly oxidizing medium.

(8) **4**: N-($CH_2CH_2CH_3$)TpClPPH; mass spectrum, *m/e* 796 (100%, MH^+ + 1) 754 (78% $TpClPPH_3^+$ + 1); ^1H NMR (CD_2Cl_2) −0.74 (3 H, t, *J* = 7.5 Hz), −1.60 (2 H, m), −4.57 (2 H, t, *J* = 7 Hz); ortho and meta H, 8–8.11 (2 H, m), 8.11–8.33 (4 H, m), 7.81 (4 H, d, *J* = 8.5 Hz), 7.67–7.9 (6 H, m); pyrrole H, 8.76 (2 H, s), 8.61 and 8.42 (4 H, AB system, *J* = 4.5 Hz), 7.43 (2 H, s).

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Free Energy Increments for Hydrogen Bonds in Nucleic Acid Base Pairs

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Contributions of hydrogen bonds to the stability of folded forms of macromolecules are not known.[1-3] Studies on small molecules have been interpreted as indicating either a favorable[4,5] or a negligible[6] free energy contribution from hydrogen bonds. Recent improvements in methods for synthesis of ribooligonucleotides permit synthesis of small double helixes with and without particular hydrogen-bonding groups.[7] For example, substitution of inosine (I) for guanosine (G) removes the 2-amino group involved in hydrogen bonding in a GC base pair. We report here thermodynamic parameters for duplex formation by self-complementary oligomers, ICCGGC, CGGCCI, ICCGG, and GGCCI. Comparison with previous results[8,9] on corresponding oligomers with I replaced by G suggests hydrogen bonds make substantial, sequence-dependent contributions to $\Delta G°$ of duplex formation.

Oligomers were synthesized as described previously[7] and purified by HPLC.[10] Thermodynamic parameters for duplex formation were derived from measurements of optical melting curves as described previously.[8,11] For a two-state transition, the inverse melting temperature in K^{-1} is related to $\Delta H°$ and $\Delta S°$ by $T_M^{-1} = (2.3R/\Delta H°) \log C_T + \Delta S°/\Delta H°$. Here C_T is total strand concentration. Appropriate plots are available as supplementary material, and results are listed in Table I. Similar results were obtained by analyzing shapes of melting curves (see Table II in supplementary material).

Empirical free energy increments for hydrogen bonds in base pairs, $\Delta\Delta G°_{HB}$, can be derived from Table I in two ways. First, $\Delta G°$'s for duplex formation by oligomers with identical core sequences but terminal GC or IC pairs can be subtracted. For example,

$$\Delta\Delta G°_{HB} = (1/2)[\Delta G°(GCCGGC) - \Delta G°(ICCGGC)] \quad (1)$$

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