and the resultant hemoglobins have oxygen affinities close to those of isolated subunits. The NMR resonance position of this hydrogen bond (–14.2 ppm) is in the range of resonance positions of 'strong' hydrogen bonds while the resonance position of the β102 asn–α94 asp proton (–10.3 ppm) appears normal [10, 21]. So energy storage for the deoxy tetramer is primarily localized in this β99 asp–α42 tyr hydrogen bond. Information between subunits is transferred through those amino acids involved in hydrogen bonding to heme pyrrole II and the innate porphyrin rigidity used to modulate porphyrin exposure to solvent which in turn controls oxygen affinity. Porphyrin sliding can also account for Fe–imidazole bond rupture in hemoglobin NO in the presence of IHP [22].

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1 M. F. Perutz, *Nature, 228,* 726 (1970).
2 M. F. Perutz, *Brit. Med. Bull., 32,* 195 (1976).
3 J. V. Kilmartin, *Brit. Med. Bull., 32,* 209 (1976).
4 J. J. Hopfield, *J. Mol. Biol., 77,* 207 (1973).
5 J. L. Hoard and W. R. Scheidt, *Proc. Nat. Acad. Sci. U.S.A., 70,* 3919 (1973).
6 A. Warshel, *Proc. Nat. Acad. Sci. U.S.A., 74,* 1789 (1977).
7 P. Eisenberger, R. G. Shulman, R. M. Kincaid, G. A. Brown and S. Ogawa, *Nature, 274,* 30 (1978).
8 G. K. Ackers, *Biophys. J., 32,* 331 (1980).
9 B. M. Hoffman and P. H. Petering, *Proc. Nat. Acad. Sci, U.S.A., 67,* 637 (1970).
10 L. C. Dickinson and J. C. W. Chien, *J. Biol. Chem., 248,* 5005 (1973).
11 K. Imai, M. Ikeda-Saito, H. Yamamoto and T. Yonetani, *J. Mol. Biol., 138,* 635 (1980).
12 M. F. Perutz, S. S. Hasnain, P. J. Duke, J. L. Sessler and J. E. Hahn, *Nature, 295,* 535 (1982).
13 P. D. Pullsinelli, *J. Mol. Biol., 74,* 57 (1973).
14 H. C. Stynes and J. A. Ibers, *J. Am. Chem. Soc., 94,* 5125 (1972).
15 H. Yamamoto, T. Takayanagi, T. Kwaan and T. Yonetani, *Bioinorg. Chem., 7,* 189 (1977).
16 E. Stellwagen, *Nature, 275,* 73 (1978).
17 M. J. Carter, L. M. Engelhardt, D. P. Rillema and F. Basolo, *J. Chem. Soc., Chem. Commun.,* 810 (1973).
18 M. J. Carter, D. P. Rillema and F. Basolo, *J. Am. Chem. Soc., 96,* 392 (1974).
19 P. W. Pettigrew, P. H. Romeo, A. Tsapis, J. Thillet, M. L. Smith, B. W. Turner and G. K. Ackers, *Proc. Nat. Acad. Sci., U.S.A., 79,* 1849 (1982).
20 K. J. Wiechelman, *U. F. Fairbanks and C. Ho, Biochemistry, 15,* 1414 (1976).
21 J. Emsley, *Chem. Soc. Rev., 9,* 91 (1980).
22 J. C. Maxwell and W. S.Caughey, *Biochemistry, 15,* 388 (1976).

Q15

^{57}Fe NMR of Iron(II) Low Spin Hemes

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Electronic structures of iron in hemoproteins have close correlation with their reactivity. Many physicochemical techniques have been applied to hemoproteins to elucidate electronic structures of heme irons. However, conclusive experimental determination of the electronic structures of low spin iron(II) heme, especially oxygenated hemes, waits for further examinations. In order to determine the electronic structures of the hemes directly from the view point of their ground state, we have started ^{57}Fe NMR studies of heme complexes in succession to our MCD [1] and *ab initio* calculation [2] on the heme complexes. ^{57}Fe NMR spectra were obtained by using steady-state free precession and the quadriga Fourier transform technique [3–5]. First, T_1 values of ^{57}Fe nuclei have been estimated for $Fe(CO)_5$ and ferrocene with natural abundance of ^{57}Fe. ^{15}N-enriched, $\alpha,\beta,\gamma,\delta$-*meso*-tetra-phenylporphine (TPP) and $\alpha,\beta,\gamma,\delta$-*meso-p*-tolylporphine (TTP) were prepared from ^{15}N-labeled pyrrole (CEA Saclay, 95% enrichment), and benzaldehyde or *p*-tolylaldehyde by the usual method [6]. Incorporation of ^{57}Fe (Spire, 95.45% enrichment) was accomplished by Rothemund's method [7]. Bis-pyridine and bis-pyrrolidine complexes of [^{15}N,^{57}Fe]-TPP and [^{15}N,^{57}Fe]-TTP with Fe(II) low spin state were prepared by a conventional method [8]. The ^{57}Fe NMR spectra recorded on a Bruker CXP-300 NMR spectrometer incorporated with a Bruker ^{57}Fe probe (using 15 mm sample tube), can be tuned between 10.2 and 9.2 MHz. The chemical shift values of the bis-pyridine complex of [^{15}N,^{57}Fe]-TPP, of the bis-pyrrolidine complex of [^{15}N,^{57}Fe]-TTP, of $K_4[Fe(CN)_6]$ and of ferrocene are 7341, 7258, 2495, and 1531 ppm low field from that of $Fe(CO)_5$ as a reference. The variation of chemical shifts of various iron(II) complexes will be discussed in terms of the d–d energy splitting in a similar way to that of ^{59}Co-complexes [9].

1 M. Hatano and T. Nozawa, in 'Advances in Biophysics., M. Kotani, S. Yomosa and M. Hatano (Eds.), Vol. 11, pp. 95–152, Japan Scientific Societies Press (1978).

2 T. Nazawa, M. Hatano, U. Nagashima, S. Obara and H. Kashiwagi, *Bull. Chem. Soc. Jpn.*, in press.

3 A. Schwenk, *Z. Phys.*, *213*, 483 (1968).

4 A. Schwenk, *J. Magn. Reson.*, *5*, 379 (1971).

5 T. Jenny, W. von Philipsborn, J. Kronenbitter and A. Schwenk, *J. Organomet. Chem.*, *205* (1981).

6 A. D. Adler, *J. Org. Chem.*, *32*, 476 (1967).

7 P. Rothemund, *J. Am. Chem. Soc.*, *70*, 1808 (1948).

8 W. M. Connor and D. K. Straub, *Inorg. Chem.*, *15*, 2289 (1976).

9 J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, *53*, 601 (1957).

Q16

Catalytic Oxidation of Hydrocarbons Using Iodosylbenzene in the Presence of a Ruthenium(III) Porphyrin Complex

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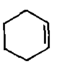
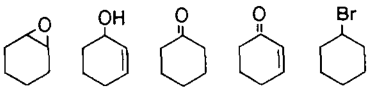
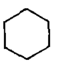
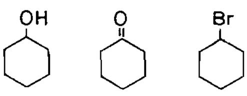
The ruthenium(III) octaethylporphyrin complex, Ru(OEP)(PPh$_3$)Br, *1*, has been prepared by the oxidation of Ru(OEP)(PPh$_3$)$_2$ [1] with excess bromine, and fully characterized by spectroscopic and crystallographic methods [2]. We have found that CH$_2$Cl$_2$ solutions of *1* (5×10^{-3} *M*) containing iodosylbenzene (0.1 *M*) catalyze at 20 °C the oxidation of certain olefins and cyclohexane (0.2–0.5 *M*). Some of the oxidation data are summarized in Table I.

Groves *et al.* [3] have reported on corresponding oxidations using iron(III) porphyrins, and have presented evidence for involvement of an oxoiron(IV) porphyrin cation–radical intermediate, O=Fe^{IV}-(porp$^{+\bullet}$). This is equivalent electronically to iron(III) plus the oxygen atom (from iodosylbenzene), and is overall at the same oxidation level as the active species in the cytochrome P-450 enzyme cycle; the enzyme systems utilize molecular O$_2$ for alkene epoxidation and hydrocarbon hydroxylation, and active O=Fe^{IV}(porp$^{+\bullet}$) intermediates have been implicated [3–5].

Studies with our ruthenium(III) system have led to isolation of closely related cation–radical species. Thus, reaction of *1* with PhIO yields a green complex tentatively formulated as O=Ru^{IV}(OEP$^{+\bullet}$)Br, *2*. A strong ESR signal at g = 2.00 (at 77 K or 20 °C), and a broad Soret band at 384 nm coupled with bands at 502 and 604 nm, are typical of cation–radical species [1, 4]; a stoichiometric spectrophotometric titration with PPh$_3$ (complex *2*: PPh$_3$ = 2.0) to give quantitatively OPPh$_3$ and [Ru^{IV}(OEP)Br]$_2$O [6] (see Scheme), and detection of bromine as cyclohexylbromide in the hydrocarbon oxidations (close to stoichiometric based on Ru, up to 85%, see Table) are consistent with the oxygen and bromine content of *2*, and with *2* being the active oxidizing species *via* free-radical reactions [1, 9, 10]:

TABLE I. Oxidation of Hydrocarbons with Iodosylbenzene Catalyzed by Ru(OEP)(PPh$_3$)Br.[a]

Substrate	Products	Yield[b]	Total turnover on metal
Styrene	Styrene oxide	21	10
Norbornene	Norbornene oxide	8	4
Cis-stilbene	Stilbene oxide	trace[c]	–
Trans-stilbene	(No reaction)		–
	 (1 : 1.7 : 0.5 : 3.4 : 0) (1 : 1.5 : 0.3 : 0.3 : 0.3)[d]	3 12[d]	1.5 6[d]
	 (1 : 8 : 9)	3.5[c]	1.7

[a]In CH$_2$Cl$_2$ at 20 °C after reaction time of 6 h. [b]Based on C$_6$H$_5$IO; this does not include loss of C$_6$H$_5$IO due to decomposition to PhI and PhIO$_2$ (~40% over 6 h). [c]As in *a*, but reaction time of 15 h. [d]In CH$_3$CN.