higher acidity of hydrogen peroxide than water (pK = 11.6 *vs.* 15.6) more than compensates for the difference in concentrations between H_2O_2 and H_2O in our experiment (about 100-fold), so that at pH 7 there is about 100-fold more OOH^- than OH^-. There are other concurrent reactions of hydrogen peroxide with the protein.[13] These will be reported in the full paper.

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The Oxidation of Iron(II) Porphyrins by Organic Molecules

Sir:

A knowledge of the nature of bond types capable of effecting the oxidation of iron(II) to iron(III) porphyrins is a requisite for formulating mechanisms of hemoprotein function. Moreover, low-valent metalloporphyrins, by virtue of their unique coordination, should be highly efficient reagents for organic synthesis.

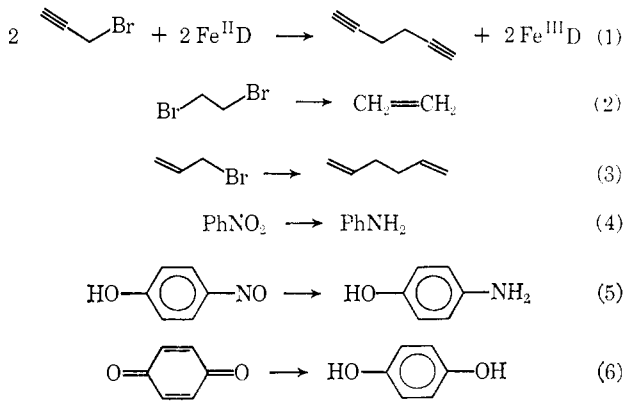
The unusually rapid rates of oxidation of iron(II) deuteroporphyrin and iron(II) protoporphyrin by alkyl halides and the stoichiometric conversion of DDT to DDD have been noted.[1] Most recently, a report of the oxidation of iron(II) porphyrins by olefins and acetylenes has appeared.[2]

We wish to outline the general nature of some rapid, quantitative room-temperature reactions of iron(II) deuteroporphyrin ($Fe^{II}D$) and its dimethyl ester with alkyl halides, quinones, and nitro and nitroso compounds and present a brief discussion of our findings. The selected illustrative cases (eq 1–6) are representative of a broad range of molecules possessing these reactive groupings. Typical reaction concentrations employed were $\sim 2 \times 10^{-3}$ M in $Fe^{II}D$ and $\sim 10^{-3}$ M substrate in 1:1 n-methylpyrrolidone–acetic acid. Calculated yields range from 97 to 100% in all cases. No other products are detectable.

It is to be emphasized that the reactive bond types reported herein were found by a very broad scan of a wide array of organic substances. In addition to peroxides, they represent the only reactive kinds of molecules encountered. The scan was conducted by injecting substrate (initial concentration 10^{-3} to 10^{-2} M) into a 10^{-4} M $Fe^{II}D$ solution under nitrogen and monitoring for the appearance of the iron(III) band at 630 mμ. The reactivity of bond types indicated by the scan were corroborated by scaling up to reaction conditions and establishing the stoichiometry.

(1) C. E. Castro, *J. Am. Chem. Soc.*, **86**, 2310 (1964).

(2) M. Tsutsui, R. A. Velapoldi, L. Hoffman, K. Suzuki, and A. Ferrari, *ibid.*, **91**, 3337 (1969).



In our system, the solvent is not so highly coordinating as to preclude any association that may be necessary for reaction. Consequently, these results *do not* accord with the reported[2] oxidative reactivity of olefins and acetylenes toward iron(II) porphyrins. Indeed we have examined some 30 olefins and acetylenes of widely differing linkage without observing oxidation by these substances. For example, the spectrum of a solution of 0.1 M methylcyclohexene and 10^{-4} M iron(II) deuteroporphyrin dimethyl ester was not altered in 8 hr.[3]

The typical coupling of halides (eq 1 and 3) is striking in contrast to the total reduction of these substances (to propylene) by "uncomplexed" metal ions like chromium(II).[4] Furthermore, the quick oxidation of $Fe^{II}D$ by quinones (eq 6), and in particular ubiquinone, is instructive. The reverse reduction of $Fe^{III}D$ by ubihydroquinone does not occur. However, this hydroquinone is a known physiological reductant of some cytochromes.[5] These results suggest that ubiquinone can function as a long-range "electron-transfer" agent at the cellular level and, further, that it is the nature of the axial ligands and the conformation of the protein about the porphyrin complex that control the redox capacities of hemoproteins toward this quinone–hydroquinone pair.

Amplified studies of each of these reactions will be reported later. Investigations of the parallel reactions with a variety of hemoproteins are under way.

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(3) For comparison, at 0.01 times the substrate concentration, the reaction with benzoquinone is complete in less than 1 sec. A trace of peroxide impurity, however, will cause oxidation and degradation of the porphyrin. With no other substrates have we observed porphyrin degradation. Hence, we believe the results reported in ref 2 are due to peroxidic impurities in the unsaturated substrates employed.

(4) C. E. Castro and W. C. Kray, Jr., *J. Am. Chem. Soc.*, **88**, 4447 (1966), and references therein.

(5) H. R. Mahler and E. H. Cordes, "Biological Chemistry," Harper and Row, New York, N. Y., 1966, pp 593–601.

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Photosensitized Aquation of Some Chromium(III) Complexes

Sir:

We wish to report the observation that aquation of various Cr(III) complexes can be photosensitized by organic compounds known to have relatively stable