

Letter

Does an Unusual Structure of Oxo-Iron Porphyrins Cause Its Stereoselective Properties?

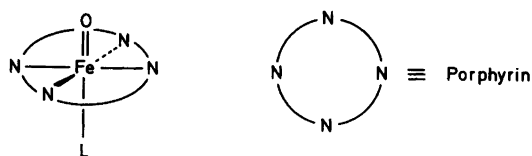
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Iron functions as the principal electron carrier in biological oxidation-reduction reactions.¹ Iron ions also serve to transport and store molecular oxygen, a function that is essential to the life of all vertebrates.¹ As to the structure of the oxygen-iron bond in hemoglobin, Collman's group has found that the oxygen binds in an end-on fashion (L. Pauling's model) to the iron of the protoheme, rather than in the sideways manner proposed by some theories.² Removal of an oxygen from hemoglobin leads to an oxo-iron(V) porphyrin, *I* which is now generally accepted to be the active oxidant in P-450 monooxygenases, catalase, peroxidase and chloroperoxidase.³

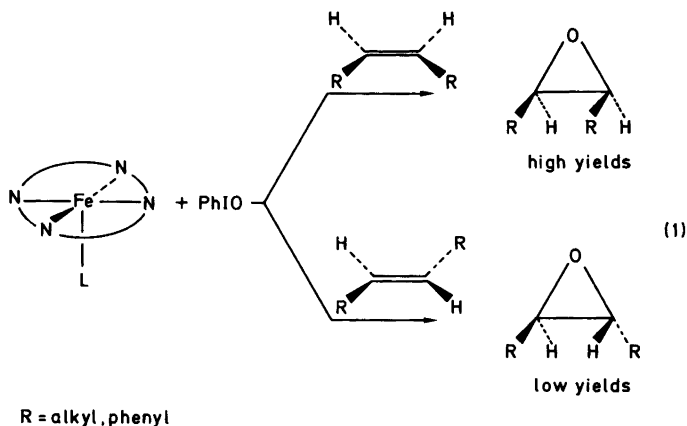
Oxo-iron(V) porphyrins, *I*, are able to hydroxylate an unactivated C–H bond in an alkene to the corresponding alcohol and to oxidize a primary alcohol to an aldehyde.³ Another important property of *I* is its stereospecific ability to ep-



1.

oxidize olefins in good yields.^{3,4} *Cis* olefins are transformed to *cis* epoxides in high yields, whereas *trans* olefins give low yields of *trans* epoxides using *I* generated, e.g., from tetraphenylporphyrinatoiron(III) chloride and iodosylbenzene⁴ (eqn. (1)).

With a high symmetry structure of the oxo-iron porphyrin, as shown in *I*, it is not quite obvious how the preferred reaction with *cis* olefins arises. The primary interaction leading to the epoxide from the olefin and *I* probably occurs between



the lone pair located on oxygen in *I*, antisymmetric with respect to the N-Fe-N plane, and the antisymmetric π^* orbital of the olefin. Thus, such an interaction between *I* and an olefin should be independent of the stereochemistry of the olefin.

Attempting to understand the stereoselectivity of oxo-iron porphyrins, it is argued that one should focus the attention on the structure of this system and the main purpose of this letter is to analyse theoretically the structure of oxo-iron porphyrin using semiempirical molecular orbital calculations⁵ in relation to its stereospecific epoxidation properties.

The structure of oxo-iron porphyrins, which has been characterized by spectroscopic and chemical analyses^{4,6} is not well established because of its instability, but is usually written as *I*.

A calculation of the molecular orbitals of *I* gives the highest occupied molecular orbitals as mainly antisymmetric combinations of d_{xz} (iron) - p_x (oxygen) and d_{yz} (iron) - p_y (oxygen) (Fig. 1). This has been used as an explanation for the instability of ferryl complexes.⁷ Among the lowest unoccupied molecular orbitals, large amplitudes of p_z character are found on the nitrogen in the porphyrin ring (Fig. 1). From the simple MO picture, it should thus be expected that a slipping motion of the oxygen towards, e.g., the right nitrogen should stabilize the system: The antibonding combination between iron and oxygen is reduced and might become bonded through inter-

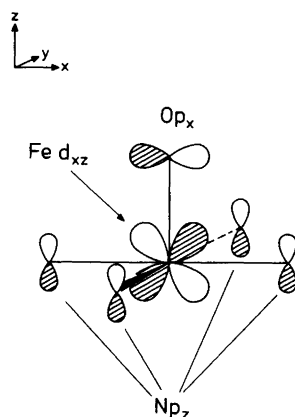


Fig. 1. The antibonding Fe d_{xz} -O p_x orbital (occupied) and the N p_z unoccupied orbitals in the porphyrin ring.

action of the two shaded loops. Furthermore, favourable interaction between the unshaded loop on oxygen (occupied) and the unshaded loop on nitrogen (unoccupied) might be possible by the slipping motion of oxygen.

A fruitful way to study the stability of oxo-iron porphyrin is to calculate an energy surface for a slipping motion of oxygen towards nitrogen by performing LCAO-MO-SCF calculations using an INDO type (intermediate neglect of differential overlap) program, which provides for transition metals.^{5b} Fig. 2 shows the calculated total

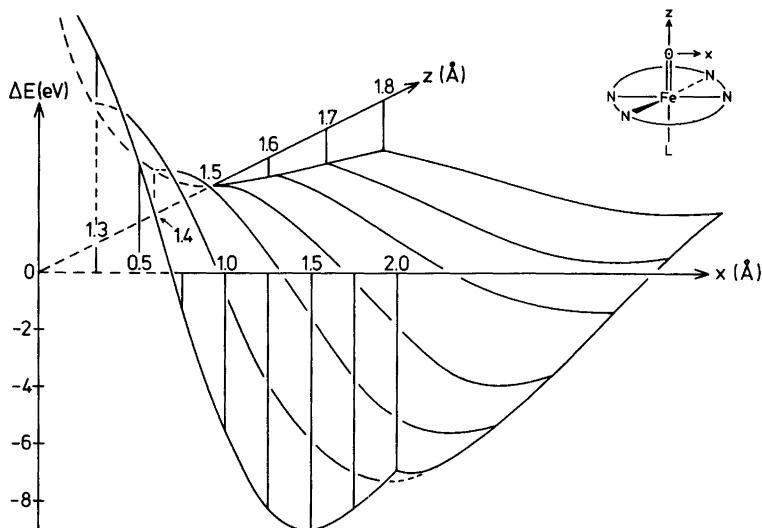
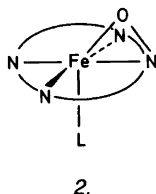


Fig. 2. The change in total energy of the oxo-iron porphyrin system as a function of the slipping motion of oxygen as indicated in the upper right corner. The energy zero is taken to be the symmetric form $x = 0 \text{ \AA}$, $z = 1.5 \text{ \AA}$.



energy surface as a function of the slipping motion of oxygen towards nitrogen (x axis) and the distance between oxygen and the iron-porphyrin plane (z axis).

It appears from Fig. 2 that the oxo-iron porphyrin system is stabilized when the oxygen moves towards the nitrogen and the minimum for the system is found in a region where the oxygen is about 1.5 Å along the x axis and 1.2 Å from the iron-porphyrin plane. This structure is shown in 2. The calculated stabilization of 2 relative to 1 is about 8 eV (~ 185 kcal \cdot mol $^{-1}$). The bond lengths for Fe–O (~ 1.9 Å) and N–O (~ 1.4 Å) do not seem unrealistic.⁸ It should also be mentioned that a determination of the energy surface in a CNDO (complete neglect of differential overlap)⁵ type of calculations gives a similar stabilization, in a geometry which is very similar to 2.

The geometry for oxo-iron porphyrin shown in 2 differs from the one usually presented in papers and textbooks.¹ It was mentioned earlier that oxo-iron porphyrins are unstable and no X-ray crystallographic structure of these compounds is available; but it might be useful here to focus on a related class of compounds – the carbene-iron porphyrin complexes which are carbon analogues of the oxo-iron porphyrin species. Such compounds have recently been synthesized^{9a} and an X-ray structure published;^{9b} the terminal carbene atom is here, in some cases, bound to both the iron atom and the pyrole nitrogen, which supports the calculated structure for oxo-iron porphyrin. Further support for structure 2 also comes from recently published X-ray structure of a nickel complex of octaethyl porphyrin N -oxide dianion, where it has been found that the oxygen is bound in the same way as in 2.^{8b} The Ni–O and N–O bond lengths in this complex are in good agreement with those found in oxo-iron porphyrin.^{8b}

With the structure of oxo-iron porphyrins suggested here, is afforded an interpretation of the stereospecific epoxidation properties: the first

step in the epoxidation of an olefin is a coordination of the olefin to the iron atom. Thus, *cis* olefins are more stable than *trans* olefins because of steric reasons. The next step is then a slipping motion of the olefin towards the oxygen and the epoxidation thus takes place via an interaction of the lowest unoccupied molecular orbital of the olefin (π^*) and the lone pair electrons on oxygen which have the same symmetry (antisymmetric).*

References

- Dugas, H. and Penney, C. *Bioorganic chemistry*. Springer-Verlag, New York 1981, p. 346 and related references.
- Collman, J. P. *Acc. Chem. Res.* 10 (1977) 265.
- Sheldon, R. A. and Kochi, J. K. *Metal-catalyzed oxidations of organic compounds*. Academic Press, New York 1981, p. 245 and references therein.
- (a) Patin, H. and Mignani, C. *J. Chem. Soc. Chem. Commun.* (1979) 685;
(b) Groves, J. T. and Nemo, T. E. *J. Amer. Chem. Soc.* 105 (1983) 5786, 5791;
(c) Dicken, C. M., Lu, F.-L., Nee, M. W. and Bruce, T. C. *J. Amer. Chem. Soc.* 107 (1985) 5776;
(d) Smith, J. R. L. and Sleath, P. R. *J. Chem. Soc. Perkin Trans. II* (1982) 1009–1015.
- (a) Pople, J. A. and Beveridge, D. L. *Approximate molecular orbital theory*. McGraw-Hill, New York 1970;
(b) Bacon, A. D. and Zerner, M. C. *Theor. Chim. Acta* 53 (1979) 21 and reference therein.
- Chin, D.-H., LaMar, G. N. Balch, A. L. *J. Amer. Chem. Soc.* 102 (1980) 4344.
- Tatsumi, K. and Hoffmann, R. *Inorg. Chem.* 20 (1981) 3771–3784.
- (a) *International tables for X-ray crystallography*. The Kynoch Press, Birmingham, UK 1962: N–O: 1.14–1.51 Å, p. 265; Fe–O: 1.94–2.31 Å, p. 269.
(b) Bach, A. L., Chan, Y.-W. and Olmstead, M. O. *J. Amer. Chem. Soc.* 107 (1985) 6510.
- (a) Mansuy, D. *Pure and Appl. Chem.* 52 (1980) 681 and references therein.
(b) Chevrier, B., Weiss, R., Lange, M., Chottart, J. C. and Mansuy, D. *J. Amer. Chem. Soc.* 103 (1981) 2899.
- Jørgensen, K. A. and Hoffmann, R. *Acta Chem. Scand. B* 40 (1986) *In press*.

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*A nearly similar mechanism has recently been suggested for the epoxidation of olefins by $\text{MO}(\text{O}_2)_2\text{L}_2$ complexes ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$).¹⁰