Acknowledgment. Funding was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. **1**, 118070-62-5; **3**, 55504-04-6; **4**, 122444-51-3; $Ph_3P{=}NPh$, 2325-27-1; $(CO)_5W(THF)$, 36477-75-5.

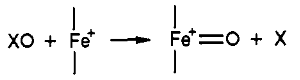
A Common Heterolytic Mechanism for Reactions of Iodosobenzenes, Peracids, Hydroperoxides, and Hydrogen Peroxide with Iron(III) Porphyrins

Teddy G. Traylor,* Wen-Pang Fann, and
Debkumar Bandyopadhyay

Department of Chemistry, D-006
University of California, San Diego
La Jolla, California 92093

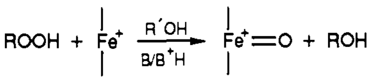
Received March 27, 1989

The isolation of high-valent iron porphyrin intermediates,[1,2] kinetic studies,[3] and product isolations[3,4] have demonstrated that the principal reaction of iron(III) porphyrins with iodosobenzenes and peracids is a two-electron oxidation to the iron(IV) radical cation (oxene) reaction 1.



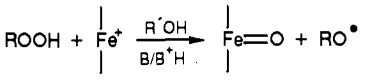
$$\text{XO} + \overset{|}{\underset{|}{\text{Fe}^{+}}} \longrightarrow \overset{|}{\underset{|}{\text{Fe}^{+}}}{=}\text{O} + \text{X} \qquad (1)$$

We find that the rate effects in reaction 2 upon changes in solvent acidity ($\text{p}K_{\text{R}'\text{OH}}$),[5b] buffer concentration[3,5b] (R'OD vs R'OH),[6b] and leaving group acidity ($\text{p}K_{\text{ROH}}$) are essentially the same for peracids and hydroperoxides.[6] These findings are consistent with similarities in mechanisms and therefore heterolytic cleavage.



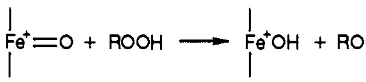
$$\text{ROOH} + \overset{|}{\underset{|}{\text{Fe}^{+}}} \xrightarrow[\text{B/B}^{+}\text{H}]{\text{R}'\text{OH}} \overset{|}{\underset{|}{\text{Fe}^{+}}}{=}\text{O} + \text{ROH} \qquad (2)$$

Bruice et al.[7] have found little effect of either buffer concentration (in water) or leaving group acidity and have concluded that hydroperoxides and hydrogen peroxide undergo homolytic cleavage under these conditions.



$$\text{ROOH} + \overset{|}{\underset{|}{\text{Fe}^{+}}} \xrightarrow[\text{B/B}^{+}\text{H}]{\text{R}'\text{OH}} \overset{|}{\underset{|}{\text{Fe}}}{=}\text{O} + \text{RO}^{\bullet} \qquad (3)$$

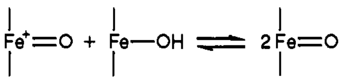
The reasons for these different results are not clear. However, available kinetic data do not provide conclusive evidence for mechanisms of cleavage. Evidence for the presence of alkoxy radicals and Fe=O, along with failures to observe hemin-catalyzed epoxidation, has also been interpreted in terms of homolytic cleavage (reaction 3).[8] However, alkoxy radicals are obtained through reactions of the oxene ($\text{Fe}^{+}{=}\text{O}$) with hydroperoxides. This and other reactions produce Fe=O.



$$\overset{|}{\underset{|}{\text{Fe}^{+}}}{=}\text{O} + \text{ROOH} \longrightarrow \overset{|}{\underset{|}{\text{Fe}^{+}}}\text{OH} + \text{ROO}^{\bullet} \qquad (4)$$

$$2\text{ROO}^{\bullet} \longrightarrow 2\text{RO}^{\bullet} + \text{O}_2 \qquad (5)$$

$$\text{RO}^{\bullet} \longrightarrow \text{R}'^{\bullet} + \text{R}''_2\text{CO} \qquad (6)$$

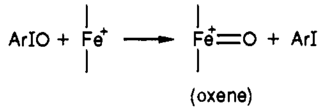


$$\overset{|}{\underset{|}{\text{Fe}^{+}}}{=}\text{O} + \overset{|}{\underset{|}{\text{Fe}}}\text{—OH} \rightleftharpoons 2\overset{|}{\underset{|}{\text{Fe}}}{=}\text{O} + \text{H}^{+} \qquad (7)$$

Furthermore we have obtained good yields of epoxide using hydroperoxides at low concentrations where reactions 4 and 5 are minimized.

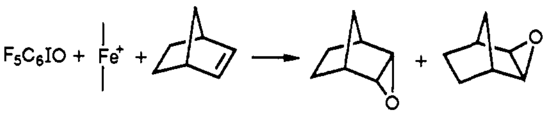
It is clear that the Fe(IV) and Fe(III) species are readily obtainable by electron-transfer reactions such as 4 or 7. However, production of the oxene $\text{Fe}^{+}{=}\text{O}$ through the endothermic reversal of such electron transfers is highly unlikely. Therefore the identification of products exclusively derived from the oxene should serve as an indication of heterolytic cleavage in the first step.

We submit the following experiments as demonstrations of the presence of $\text{Fe}^{+}{=}\text{O}$, assuming that the isolation of the oxene from reaction of iron(III) porphyrins with iodosobenzene[1] unequivocally establishes reaction 8.



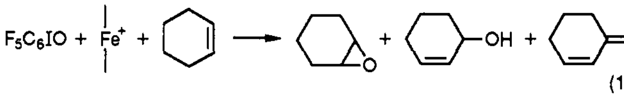
$$\text{ArIO} + \overset{|}{\underset{|}{\text{Fe}^{+}}} \longrightarrow \underset{\text{(oxene)}}{\overset{|}{\underset{|}{\text{Fe}^{+}}}{=}\text{O}} + \text{ArI} \qquad (8)$$

We have found that the epoxidation of norbornene by use of the oxene from reaction 8 produces a mixture of products which is at once unlike that from any other epoxidation process and specific for the particular metalloporphyrin catalyst.[11] In particular, this is the only reaction which gives any appreciable endo product.



(9)

Among many other reactions which display product compositions specific for the *oxene* of a particular metalloporphyrin are the opening of hexamethyldewarbenzene[13] and epoxidation of cyclohexene.[12]



(10)

Thus, for example, with the catalyst iron(III) tetrakis(2,6-dichlorophenyl)porphyrin chloride (TDCPPFeCl) the product contains only 4–5% of alcohol or ketone.[12a] Other catalysts give different ratios, just as in the case of norbornene epoxidation.[12a,b] It is known that peroxy radicals give principally hydrogen abstraction from cyclohexene.[14]

We have therefore adopted known methods of producing alternatively the oxene, the oxo species, and peroxy radicals in the presence of these alkenes and compared the product compositions with those obtained from reactions of the same iron porphyrin

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(9) For example, although the "2,4,6-tri-*tert*-butylphenol trap" method,[3,10] for following the rates of reaction of hemins with ROOH, affords accurate kinetics with peracids, it often leads to inconsistent kinetic constants with hydroperoxides, especially in the absence of proximal imidazole or buffers.

(10) Lee, W. A. Thesis, University of California, San Diego, 1983.

(11) Thus, the Cr(III), Mn(III), and Fe(III) complexes of tetraphenylporphyrin give exo/endo epoxynorbornane ratios of 1000, 350, and 55, respectively,[12] compared to 10 for the catalyst used here (all in dichloromethane).

(12) (a) Traylor, T. G.; Miksztal, A. R. *J. Am. Chem. Soc.*, in press. (b) Traylor, T. G.; Nakano, T.; Dunlap, B. E.; Traylor, P. S.; Dolphin, D. *J. Am. Chem. Soc.* **1986**, *108*, 2782.

(13) Traylor, T. G.; Miksztal, A. R. *J. Am. Chem. Soc.* **1987**, *109*, 2770.

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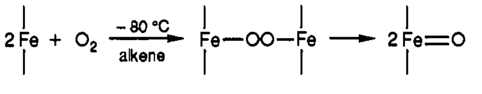
Table I. Products of Oxidation of Norbornene and Cyclohexene by Various Oxidation Systems[a]

oxidant	intermediate	norbornene exo/endo[b]	cyclohexene epox/alc[c]	cyclohexene epox/(alc + ketone)
PFIB, TDCPPFeCl	$Fe^+{=}O$	13 (15%)[d]	27 (50%)[d]	20
O_2, TPPFe[e]	$Fe{=}O$	(0%)[d]	(0%)[d]	(0%)[d]
PFIB, *t*-BuOOH	*t*-BuOO•	>58[f] (4%)[d]	2.9 (3%)[d]	1.4
H_2O_2, TDCPPFeCl		18 (25%)[d]	26 (50%)[d]	15
t-BuOOH, TDCPPFeCl		15 (16%)[d]	13[g] (16%)	11

[a] The reaction solution contained 1 M alkene, 0.2 M in oxidant, and 0.001 M catalyst in a solvent containing 59.3% CH_2Cl_2, 39.3% methanol, and 1.4% water by volume except for the reaction with O_2. TDCPPFeCl: iron(III) tetrakis(2,6-dichlorophenyl)porphyrin chloride. [b] The ratio of *exo*-2,3-epoxynorbornane to *endo*-2,3-epoxynorbornane. The epoxides were identified by GC-mass spectroscopy. [c] The ratio of epoxycyclohexane to 2-cyclohexene-1-ol. [d] Total yields of all products, based upon oxidant are given in parentheses. All yields are corrected for response factors and compared to an internal standard with use of gas liquid chromatography. Yields were not optimized. Much higher yields have been obtained in all the catalyzed reactions by varying conditions. Cyclohexenone always accompanied cyclohexanol. [e] The oxo compound was generated at –80 °C in toluene as solvent in the presence of 3×10^{-3} M iron(II) tetraphenylporphyrin, 1 M alkene, or in phosphine and warmed to room temperature as described by Balch et al.[2] [f] Using peroxy radicals produced in other ways exo/endo ratios were ~1000. [g] Both the yield of epoxide, which disappears with time, and the epoxide/alcohol ratio are very sensitive to traces of oxygen under these conditions. It is difficult to prevent at least some autoxidation of cyclohexene since O_2 is evolved in the side reactions 3 and 4. Without freeze/thaw degassing, lower epoxide/alcohol ratios are observed.

with hydrogen peroxide or *tert*-butyl hydroperoxide. The methods used are reaction 8,[1] reaction 11,[2] and reaction 12.[5]



$$2\,\mathrm{Fe} + \mathrm{O_2} \xrightarrow[\text{alkene}]{-80\,^\circ\mathrm{C}} \mathrm{Fe{-}OO{-}Fe} \longrightarrow 2\,\mathrm{Fe{=}O} \qquad (11)$$

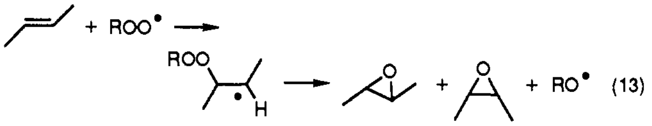
$$\mathrm{F_5C_6IO} + 2t\text{-}\mathrm{BuOOH} \longrightarrow \mathrm{F_5C_6I} + 2t\text{-}\mathrm{BuOO^\bullet} + \mathrm{H_2O} \qquad (12)$$

We first repeated the preparation of $Fe{=}O$ described by Balch et al.[2] and obtained his results, both with respect to phosphine oxidation and the failure to obtain epoxide from alkenes. Reaction 12 has been shown both by Milas et al.[15] and in our laboratories to afford *t*-BuOO• radicals.

Except for the formation of the oxo species, which were produced exactly as described by Balch et al., all of the oxidations were carried out at room temperature in the same solvent.

The results are given in Table I. The conclusions are clear. The reactions of hydrogen peroxide or *tert*-butylhydroperoxide with TDCPPFeCl produce essentially the same exo/endo epoxynorbornane ratios and epoxycyclohexane/cyclohexenol ratios as does the reaction with PFIB. The oxo species affords no epoxide, and the *tert*-butyl peroxy radical gives essentially *no* endo epoxide. This, we propose, is evidence that at least that portion of the reaction which produces oxidized products proceeds by *heterolytic cleavage* of hydrogen peroxide or *tert*-butyl hydroperoxide.

The differences in kinetic results among different laboratories[3,7] and previous failures to obtain epoxides from hydrogen peroxide or hydroperoxides[16] are now becoming clear. The catalase reaction 3 prevents epoxidation and/or leads to loss of stereochemistry.



(13)

Additionally, the consequent buildup of alkylperoxy and alkoxy radicals which occurs only with hydroperoxides leads to reactions of these radicals with the products used to detect rates[3,17] and significant errors can result.[3,9,17]

Apparently, more electronegative oxenes are less selective toward reaction 3 with hydroperoxides and allow higher yields of epoxides from hydrogen peroxide. All of the reactions of the oxidants RIO, RCO_3H, ROOH, and H_2O_2 with TDCPPFeCl in hydroxylic solvents are now understandable as heterolytic processes like those which occur in peroxidase and catalase. The importance of these conclusions is that we are encouraged to explore methods of obtaining high yield, stereo- and regiospecific catalytic epoxidation using hydrogen peroxide and hydroperoxides. These studies will be reported elsewhere.

Acknowledgment. Support for this work by the National Science Foundation (Grant CHE87-21364) is gratefully acknowledged. Helpful discussion with and the preparation of the catalyst by Dr. Shinji Tsuchiya are also appreciated.

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(18) Hydroperoxides in contrast to peracids or hydrogen peroxide are particularly prone to a variety of free radical chain processes. Since either $Fe{=}O$ or $Fe^+{=}O$ can initiate such processes, it becomes difficult to establish the mechanism of the initial reaction under conditions where these chain reactions (evidenced by RO• cleavage, O_2 evolution, peroxy radical addition, etc.) are present. We suggest that this is responsible for the suggestion[7] that peracids react by heterolytic cleavage and hydroperoxides by homolytic cleavage. In fact, our studies along with those of Groves et al.[19] and Balch et al.[20] indicate that the change from heterolytic to homolytic cleavage occurs with both peracids and hydroperoxides at a point where general acid catalysis becomes ineffective. Thus in basic media or in the absence of hydroxylic solvents homolytic cleavage is to be expected. In hydroxylic solvents all the reactions appear to be heterolytic with the catalysts we have used.

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Evidence for a Double-Minimum Potential for Intramolecular Hydrogen Bonds of Aqueous Hydrogen Maleate and Hydrogen Phthalate Anions

Charles L. Perrin* and John D. Thoburn

Department of Chemistry, D-006
University of California, San Diego
La Jolla, California 92093

Received January 9, 1989

In the study of hydrogen bonds one of the fundamental questions is whether the potential energy for motion of the hydrogen has a single minimum (**1a**) or two minima (**1b**). If single, the hydrogen is fixed between the two donor atoms. If there are two minima, the hydrogen will be found closer to one donor than to the other, even if those donors are identical. There are then two forms in rapid equilibrium (**1b**). Both situations have been observed by a variety of experimental methods.[1] One direct method for distinguishing them is the method of isotopic perturbation of degenerate equilibrium.[2] Saunders and Handler[3] have applied

$$-\mathrm{O}\cdot\cdot\mathrm{H}\cdot\cdot\mathrm{O}- \qquad\qquad -\mathrm{O}-\mathrm{H}\cdots\mathrm{O}- \rightleftharpoons -\mathrm{O}\cdots\mathrm{H}-\mathrm{O}-$$

1a **1b**

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