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Selective Oxygen Transfers with Iron(III) Porphyrin Nitrite

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The reaction of octaethylporphyrin iron(III) chloride with potassium crown ether (18-crown-6) nitrite in *N*-methylpyrrolidone−1% acetic acid under argon generates the iron(III) nitrite salt ($PFeNO_2$). The latter is a unique and selective oxygen atom transfer reagent. The reaction of a broad range of substrates (S) proceeds quantitatively to yield the oxidized substrate and the iron(II) porphyrin−nitrosyl adduct: $PFeNO_2 + S \rightarrow PFeNO + SO$. Diatomic molecules to which oxygen is directly transferred from $PFeNO_2$ are NO, CO, and O_2. The conversion NO to NO_2 is shown via $^{15}NO_2^-$ labeling experiments to proceed exclusively by the O atom transfer process. The ozone, generated from dioxygen, was trapped with nitrite ion and the two olefins 2-methyl-2 butene and 2,3-dimethyl-2 butene. These substances are inert to $PFeNO_2$ under argon. However, in an oxygen-saturated reaction mixture, nitrite produced nitrate. The olefins, following reduction of the reaction mixture with Zn/HOAc, yielded 1 mol of acetone and acetaldehyde and 2 mol of acetone, respectively. Other simple O atom transfers under argon were observed with dimethyl sulfide and triphenylphosphine. The $PFeNO_2$ reagent shows a preference for O insertion into allylic, benzylic, and aldehydic C−H bonds. Thus, no olefin containing these moieties is epoxidized. However, styrene and *cis*-stilbene are converted to styrene oxide and *cis*-stilbene oxide, respectively. The double oxidation of allylbenzene to *trans*-cinnamaldehyde entails an allylic rearrangement that suggests radical character to the O insertion process. However, no kinetic evidence for this was obtained. The reaction is an overall third-order process, rate $= k(PFe^{III})(NO_2^-)(S)$. There was no correlation of observed rates with relevant C−H bond dissociation energies of substrates. The fastest reacting substrate was nitric oxide ($k_{22}° = 52\ M^{-2}\ s^{-1}$) and the slowest was toluene ($k_{50}° = 6.3 \times 10^{-4}\ M^{-2}\ s^{-1}$). The range and selectivity of these O atom transfers sets them apart from the catalytic oxidations brought about by reactions of iron(III) porphyrins with peroxides, iodosoaryls, hypochlorite, and other oxidants. The driving force for the relatively mild oxidations with $PFeNO_2$ resides in the thermodynamic stability of the heme−NO adduct. Given the broad presence of nitrite in the environment and the ubiquity of porphyrins in the biosphere, the activation of nitrite by iron porphyrins has both an environmental and biochemical significance.

Introduction

The epoxidation of olefins by a combination of iron(III) porphyrin and various oxidants has been studied extensively in the past two decades as a biomimetic model for cytochrome P450.[1] Following the initial report by Groves and colleagues,[2] with iron(III)TPP and iodosobenzene, corresponding research has expanded at an astonishing rate, and this work has contributed to the resurgence of interest in biological processes by organic and inorganic chemists. Generally, the porphyrins employed have been TPP derivatives. The oxidants have included principally iodosoaryls,[3] perbenzoic acids,[4] alkyl and acyl hydroperoxides,[5] amine oxides,[6] persulfate,[7] and hypchlorite ion.[8] These reactions have been conducted with the oxidant in large excess such that the reaction is catalytic in iron porphyrin. Systems with oxidation-resistant porphyrins, notably 2,6-dichlorophenyl- and pentafluorophenyl-TPP derivatives,[9,10] in some cases along with pentafluoroiodosobenzene, exhibit particularly high turnovers. Moreover, a variety of other transition metals have been employed successfully in these reactions.[1,11] In addition to epoxidation, the metalloporphyrin−oxidant reagents are capable of O atom insertion into C−H bonds,[12] and the conversion of sulfides to the corresponding oxides.[13] Mechanistic kinetic[3,14] and spectral[15] studies point to metal−oxo and metal−oxo porphy-

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rin cation radicals as intermediates in these processes. However, recent work with efficient cation−radical traps,[16] with zinc porphyrins,[17] and water exchange studies challenge this formulation.

As a part of our studies of the redox reactions of iron porphyrins[18] and hemeproteins[19] with N−O-bonded species, we have reported a stoichiometric oxygen atom transfer from porphyrin iron−NO_2 adducts to a range of substrates under argon.[20] In this work we expand upon these preliminary findings and attempt to place this new reaction in the general framework of porphyrin wrought oxidation chemistry.

Results and Discussion

Stoichiometry. The general chemistry described in this work proceeds according to the stoichiometry shown in eqn 1 (P = porphyrin, S = substrate). Starting

$$PFe^{III} + NO_2^- \overset{K}{\rightleftharpoons} PFeNO_2 \xrightarrow[k_{rate}]{S} PFeNO + SO \quad (1)$$

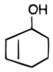
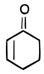
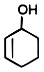
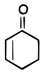
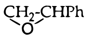
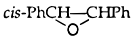
reactants are chloroiron(III) octaethylporphyrin, potassium crown ether (18-crown-6) nitrite, and substrate. The oxidized substrate and the porphyrin iron(II) porphyrin−nitrosyl adduct are generated in each case. Reactions were conducted under argon in the solvent *N*-methylpyrrolidone−1% acetic acid. An exception is the reaction with oxygen. This was conducted in an oxygen-saturated vessel. Products and yields are summarized in Table 1.

In addition to the substances listed in Table 1, the following were found to be inert under these conditions (no reaction in 36 h): 2-methyl-2-butene, 2,3-dimethyl-2-butene, vinyl chloride, *cis*- and *trans*-1,2-dichloroethene, *trans*-stilbene, and nitrite ion.

The reactions feature (i) direct oxygen atom transfers to the diatomic gases NO, O_2, and CO, as well as to triphenylphosphine and dimethyl sulfide (lines 1−5); (ii) a preference for allylic, benzylic, and aldehydic C−H insertion (lines 6−14); and (iii) the epoxidation of olefins not containing an allylic or aldehydic C−H bond (lines 15−16). Some aspects of each of these reactions require further comment.

The Diatomic Gases. These oxygen transfers set the reactions of the PFe^{III}/NO_2^- system apart from those of the iron porphyrin-catalyzed peroxide oxidations noted in the Introduction. As far as we are aware, the latter reagents do not bring about these transformations. The $CO-CO_2$ conversion is straightforward. However, the NO and O_2 oxidations need further characterization.

Table 1. Oxidations with Chloroiron(III)octaethylporphyrin and Potassium (18-Crown-6) Nitrite in NMP−1%HOAc under Argon at 22 °C

Substrate	Products	Yield[a]	Characterizn
NO	NO_2	100	GC, NO_3^- from prod. gases
O_2	O_3	100	NO_2^- oxidn.olefin trap[b]
^{13}CO	$^{13}CO_2$	100	$H^{13}CO_3^-$, ^{13}C-nmr
Ph_3P	Ph_3PO	100	^{31}P-nmr
Me_2S	Me_2SO	90	GC, GC-MS
CH_3CH_2CHO	$CH_3CH_2CO_2H$	95	GC,GC-MS[c]
PhCHO	$PhCO_2H$	95	GC-GCMS[c]
$CH_2=CHCH_2Cl$	$CH_2=CHCHO$	112	GC, GC-MS,IR
$CH_2=CHCH_2Ph$	*trans*-PhCH=CHCHO	100[d]	GC-MS,IR
$PhCH(CH_3)_2$	$PhCHOH(CH_3)_2$	100	GC-MS
$PhCH_3$	$PhCH_2OH$	100	GC-MS
$CH_2=CHCH_2)_2$	$CH_2=CHCH_2CH=CHCH_2OH$(?)		GC-MS
		90	GC-MS
		10	GC-MS
		100	GC-MS
$CH_2=CHPh$	 CH_2-CHPh (O bridged)	35	GC-MS,IR
	$PhCH_2CHO$	65	GC-MS,IR
cis-PhCH=CHPh	 *cis*-PhCH—CHPh (O bridged)	100	GC-MS

[a] In percent. 100(moles of product/moles of PFe^{III}). [b] See text. [c] Of TMS ester. [d] 100(moles of product/2 moles of PFe^{III}).

NO−NO_2. As detailed in the Experimental Section, the reaction proceeds according to the general stoichiometry indicated in eq 1. In this case the reaction is (eq 2):

$$PFeNO_2 + NO \rightarrow PFeNO + NO_2 \quad (2)$$

The stoichiometry alone, however, does not establish that an oxygen atom transfer from the nitrite adduct has occurred. NO is the only substrate studied that is both a substrate and product. Thus, in this case, assuming there is some iron(II) character to the iron(III)−nitrite adduct (PFe^{III+}, $NO_2^- \leftrightarrow$ PFeII, NO_2), the reaction (eq 2) could represent a simple ligand exchange. In order to address this and other potential schemes that may explain these results, the NO oxidation was conducted with the ^{15}N-labeled nitrite salt.[21] Thus, an oxygen atom transfer (eq 3) must result in ^{15}NO but *no* $^{15}NO_2$.

$$PFe^{III+} + {}^{15}NO_2^- \rightarrow PFe^{15}NO_2 \xrightarrow{NO} PFe^{15}NO + NO_2 \quad (3)$$

Analysis of the product gases by mass spectroscopy and by ^{15}N-NMR of an aqueous solution into which they were passed agreed exactly with this occurrence. The mass spectra of a sample stored in an evacuated tube and one

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(21) A nitrogen rather than oxygen label was selected because the former can give an all or nothing result, and it is subject to both MS and NMR analysis.

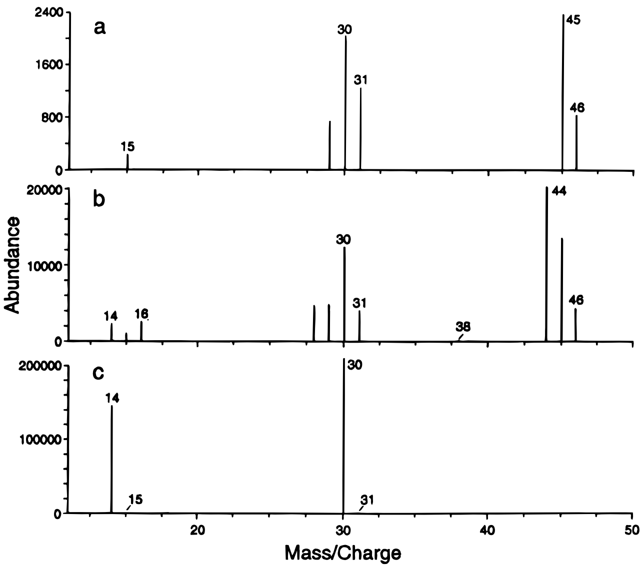

Figure 1. Mass spectra for the reaction gases from PFe^{III}, $^{15}NO_2^-$, and NO: (a) stored gas sample, (b) sample taken directly above liquid in reaction and analyzed immediately, (c) sample of NO.

Table 2. Relative Mass Spectral Intensities for NO and NO_2 from the $^{15}NO_2^-$ Exchange Experiments

sample	$NO_{(30)}$	$^{15}NO_{(31)}$	$NO_{2(46)}$
4[a]	52	32	20
5[b]	37	13	13
6[b,c]	31	12	10
7[b,c]	31	12	10
8[d]	60	1	

[a] Reaction gas from stored sample. [b] Reaction gas, just above liquid, directly analyzed. [c] Intensities from single ion monitoring for masses 30, 31, 46, and 47. [d] The NO reference.

taken directly from a reaction mixture via gas tight syringe and immediately injected into the mass spectrometer are shown in Figure 1. In both cases masses for ^{14}NO and ^{15}NO (30 and 31) are apparent along with a mass for $^{14}NO_2$ (46). No mass at 47 was observed in any sample. A reference spectrum of pure NO, obtained in similar fashion, establishes the validity of the experimental technique (no oxygen oxidation of NO). The relative intensities of the relevant ions from four runs and the NO standard are shown in Table 2.

There is consistency to these analyses. ^{15}NO is generated. $^{15}NO_2$ is not. The ability to see the ^{15}NO in the gas phase is the result of the equilibrium between iron-bound NO in solution and the excess nonlabeled NO in the gas and solution phases (eq 4).

$$PFe^{15}NO + NO = PFeNO + {}^{15}NO \qquad (4)$$

For NMR analyses, following completion of a $^{15}NO_2^-$/NO reaction, the mixture was purged with argon, and effluent gases were passed through D_2O. The volume of the latter was chosen such that the concentration of nitrite and nitrate from the rapid hydrolysis[22] of NO_2 (N_2O_4, eq 5) would be 0.02 M.

$$2NO_2 = N_2O_4 \xrightarrow{H_2O} NO_2^- + NO_3^- + 2\,H^+ \qquad (5)$$

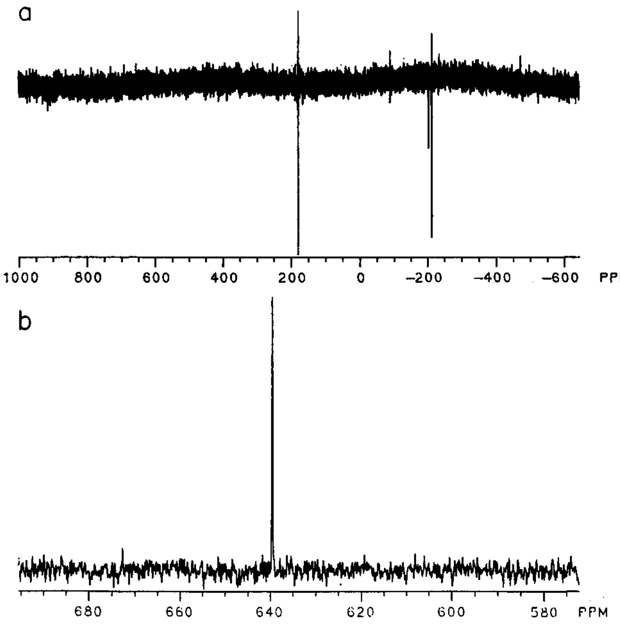

Figure 2. ^{15}N-NMR of (a) product gases bubbled through D_2O; (b) standard 0.02 M D_2O solution of K (crown ether) $^{15}NO_2$.

The ^{15}N-NMR spectra of this aqueous solution is compared with that of a 0.02 M solution of the potassium-(18-crown-6) ^{15}N-nitrite, used in these reactions, in Figure 2. The aqueous solution from the reaction shows only the resonances for the ^{15}N-benzamide (nondecoupled) added as a reference. Thus, in agreement with the mass spectral findings no $^{15}NO_2$ is generated in these reactions. In sum, these results establish that an O atom transfer from $PFeNO_2$ to NO does occur.

O_2−O_3. Three reactants were chosen to demonstrate the generation of ozone in these reactions. They were nitrite ion, and the two olefins 2-methyl-2-butene and 2,3-dimethyl-2-butene. A preliminary account of this work has recently appeared.[20b] None of these substances are substrates for the PFe^{III}/NO_2^- reaction under argon. However, nitrite[23] and the olefins[24] are efficient scavengers of ozone. Derived products are well established and, with the olefins, are uniquely characteristic of ozone. The splitting of olefins by the sequence ozonolysis followed by reduction with zinc and acetic acid is the classical procedure for locating the position of double bonds in unknown structures. Reactions were conducted in the general manner outlined above (Table 1) except a thoroughly oxygen-purged and saturated system under slight oxygen pressure (10 mm) was employed. With nitrite as the ozone trap, following reaction, the mixture was concentrated and nitrite and nitrate were analyzed in an aqueous extract. The total recovery of nitrite and nitrate was 73%, and the nitrate/nitrite ratio was 0.5 ± 0.1 (theoretical, 0.6). The presence of nitrate was confirmed by infrared analysis (1350 cm^{-1}). With the olefin traps, a large excess of olefin was employed to compete with the nitrite oxidation. Following reaction, the mixture was purged with argon and stirred with powdered zinc and additional acetic acid for 3 h. The mix was then distilled at low temperature (<60 °C), and the distillate was analyzed by GC, GC−MS, and IR. The yield of

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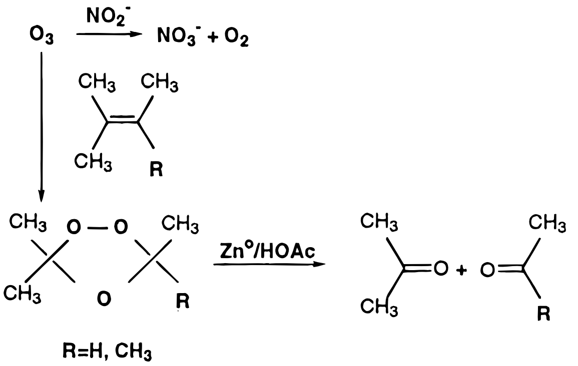
acetone from 2,3-dimethyl-2-butene was 100 ± 5% (2 mol of acetone/mol PFe^{III}). A corresponding reaction sequence with 2-methyl-2-butene yielded 1 mol of acetone and 1 mol of acetaldehyde. The latter were confirmed by mass spectral and infrared analysis. Thus, ozone is trapped from these reactions in an oxygen atmosphere. These results are summarized in eqs 6 and 7.

$$PFeNO_2 + O_2 \rightleftharpoons PFeNO + O_3 \qquad (6)$$



(7)

We presume reaction (6) is reversible. Though stable in air for hours, the iron(II)−NO adduct is not stable in an oxygen saturated environment.

The C−H Insertions. Reactions with allyl chloride, allylbenzene, and cyclohexene are striking in that they show no products derived from olefin epoxidation. Rather, the products result from allylic C−H insertion exclusively. With allyl chloride, the first formed halohydrin loses HCl to yield acrolein directly (eq 8). Note, epichlorohydrin, the product of epoxidation, could not be detected in the reaction mixture, and it is not transformed to acrolein under these conditions.

$$CH_2{=}CHCH_2{-}Cl \xrightarrow{PFe^{III}NO_2^-} (CH_2{=}CHCH(OH){-}Cl) \rightarrow CH_2{=}CHCHO + HCl \qquad (8)$$

The *trans*-cinnamaldehyde resulting from allylbenzene is surprising. There are several explanations for this. We believe the simplest is that this results from a second O insertion into the rearranged allylic alcohol. The result suggests an allyl radical intermediate and some radical character to the O insertion process[25] (eq 9).

$$CH_2{=}CHCH_2Ph \rightarrow HOCH_2CH{=}CHPh \rightarrow \textit{trans}\text{-}PhCH{=}CHCHO \qquad (9)$$

The reactions with cyclohexenol and cylclohexene again express the selectivity of the reagent for allylic C−H insertion rather than epoxidation, and the results with cumene and toluene are in accord with oxygen insertion into activated C−H bonds. The olefin 1,5-hexadiene yields a product that was not fully characterized. However, the mass spectrum of it is consistent with the terminal allylic alcohol (1-hydroxy-2,5-hexadiene). The results with the olefins differ markedly from the general pattern of epoxidation observed with the peroxide−iron porphyrin reagents.

Epoxidations. The epoxidation of styrene and subsequent rearrangement of the oxide (upon standing in the reaction mixture and upon gas chromatography) to phenylacetaldehyde is straightforward and has also been reported with the PFe^{III}/ArIO system.[1] The successful reaction with *cis*-stilbene, but the lack of reaction of the trans isomer, suggests some steric constraint in approaching the iron porphyrin -bound NO_2. The single product here is in contrast to the variety of substances observed with PFe^{III}/ArIO.[10]

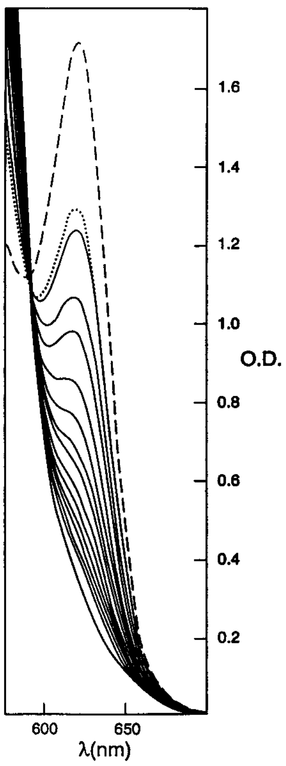


Figure 3. Repeat spectral scans of NO reaction, $(PFe^{III})_o = 3.7 \times 10^{-4}$ M, $(NO)_o = 3.7 \times 10^{-3}$ M, $(NO_2^-)_o = 7.4 \times 10^{-3}$ M: (- - -), PFe^{III}, (···) at 51 s, final PFeNO lowest spectrum.

Kinetics. The general features of the visible spectrum associated with the conversion of iron(III) porphyrin to iron(II) nitrosyl adduct by triphenylphosphine have been previously presented.[20] We show in this work only the diminution of the iron(III) band at 619 nm attendant upon the addition of NO to the nitrite−iron(III) solution (Figure 3). A pseudo-first-order plot of the data is shown in Figure 4. These reactions are overall third order (eq 10). This is in agreement with the formulation given in

$$-d(PFe^{III})/dt = d(PFeNO)/dt = k(PFe^{III})(NO_2^-)(S) \qquad (10)$$

eq 1, wherein $k = k_{rate}K_{eq}$. NO is the fastest reacting substrate, and the overall third-order rate constant for it at 22 °C is 52 $L^2/mol^2/s$. A typical plot for cumene, one of the slower reacting hydrocarbons, is shown in Figure 5.

The rate constants for selected substrates are given in Table 3, along with the relevant bond dissociation energies. For the relatively slow C−H insertions, kinetics were monitored at 50 °C. The reproducibility of rate constants evaluated in this manner was ±20% run to run.

While all of the C−H oxygen insertions are much slower than the direct oxygen atom transfers to NO or triphenylphosphine, there is clearly no correlation of these rates with available C−H bond dissociation energies. However, it is unknown to what extent the various substrates may have influenced the equilibrium between

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(25) An allylic C−H abstraction followed by HO return to the terminal carbon.

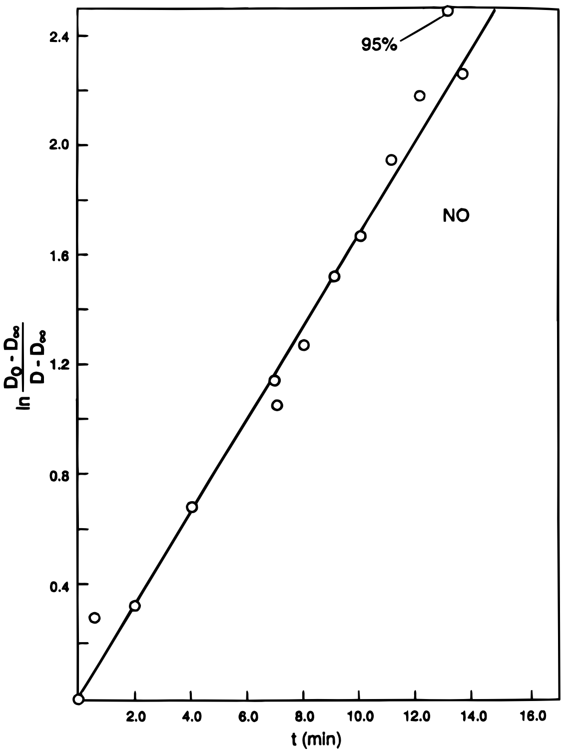

Figure 4. Pseudo-first-order plot of the data in Figure 3.

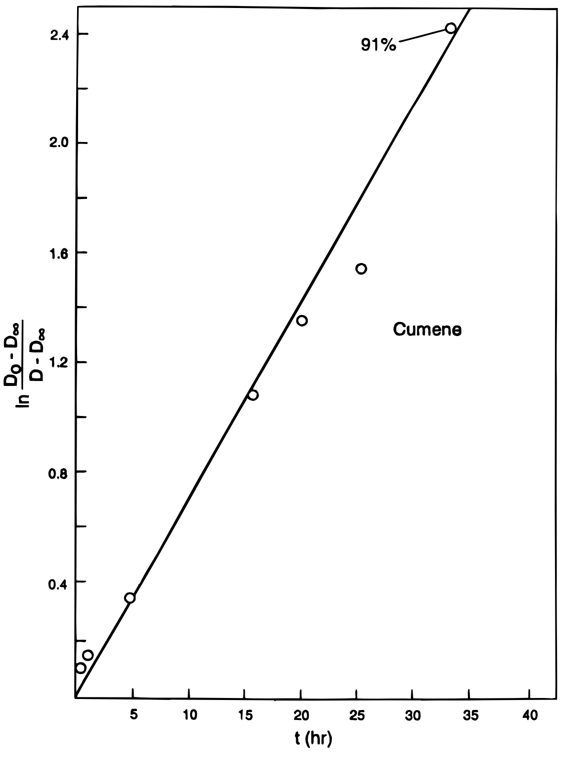

Figure 5. Pseudo-first-order plot for cumene.

Table 3. Rate Constants for Reaction of Various Substrates with Chloroiron(III) Octarthylporphyrin with Potassium Crown Ether (18-Crown-6) Nitrite in NMP^a−1%HOAc at 50 °C

substrate	k (M^{-2} s^{-1}) × 10^3	D_{C-H} (kcal/mol)^b
NO	52 000^c	
triphenylphosphine	1300^{c,20}	
allyl chloride	190	89
propionaldehyde	45	87
cumene	45	84
benzaldehyde	5.8	87
allyl benzene	3.8	
cyclohexene	3.5	
toluene	0.63	88

^{a} NMP = *N*-methylpyrrolidone. ^{b} At 25 °C.[37] ^{c} At 22 °C.

PFe^{III} and $PFeNO_2$. The starting iron(III) spectrum in Figure 2 exhibits a λ_{max} at 619 nm. This is shifted from the 627 nm observed for the chloroiron(III) porphyrin in this solvent. The relatively high concentrations of porphyrin (3.7×10^{-4} M) and nitrite salt (7.4×10^{-3} M) suggest that this spectral shift reflects the generation of the iron(III)−nitrite or it represents a significant dissociation of chloride from the inner coordination sphere of iron (a salt effect). Potentiometric analyses for chloride[26] indicate it is completely dissociated under the conditions employed for kinetic analysis. Given that nitrite is in the rate law, we infer the initial equilibrium (eq 1) is between porphyrin−iron−solvate and nitrite ion. Thus, the kinetics are consistent with a rate-limiting step that entails all three reactants, but we have no evidence, for the C−H insertion reactions, to suggest there is significant C−H bond cleavage in the transition state.

Thermodynamics. At this time, it is not possible to assess accurately the thermodynamics of these reactions. The true stability of the free heme−NO adduct, though high, is unknown. It is considered to be formed "irreversibly", and the rate of its dissociation has been approximated as 0.[27d] The nonavailability of other relevant thermodynamic factors in this solvent is also complicating. However, any crude approximation of free energies for reaction of the diatomic gases, based on the data at hand (and an assumed dissociation rate of 10^{-6} s^{-1} for heme−NO), would indicate the NO and CO oxidations are thermodynamically favorable, but the O_2 to O_3 reaction is not. Thus, we assume the equilibrium in eq 6 may lie far to the left. This would be in keeping with the fast reaction of O_3 with NO in the gas phase.[28] Presumably then this reaction occurs because the products are removed by further reaction.

In our view, the porphyrin iron(III)−nitrite salt exhibits a broader spectrum of reactivity than the corresponding metalloporphyrin−peroxide systems, but it appears to be less reactive with hydrocarbons and more selective. With olefins, it exhibits a preference for allylic and benzylic C−H oxygen atom insertion over epoxidation. It shows none of the properties of a peroxide or "HO^+" type of reagent.

The prevalence of nitrite in the environment, and the ubiquitousness of iron porphyrins in the biosphere, imparts an environmental relevance to this work. As an example, tissue or other structural damage could result *in vivo* via the ozone reaction. Moreover, the oxidation and hydrolysis of nitric oxide to nitrite[22,29] may well occur at sites near its generation. That is, NO synthase is a P450-like hemeprotein,[30] and oxygen is a requisite for reaction. Thus, other oxidative processes proceeding via $PFe^{III}NO_2$ are possible. In addition, nitrogen dioxide is

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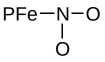
a well-known air pollutant, and it is acutely toxic.[31] It is an interesting question whether or not an entity similar to the iron−nitrite generated herein could result from the reaction of NO_2 (N_2O_4) with iron(II) porphyrin (eq 11):

$$\mathrm{PFe^{III} + NO_2^- \rightarrow PFeNO_2 \overset{?}{\leftarrow} PFe^{II} + NO_2} \quad (11)$$

The X-ray structures[32] of sterically encumbered iron porphyrin−nitrites establish the bonding of the nitro ligand to iron is through nitrogen:



$$\mathrm{PFe{-}\underset{\displaystyle O}{\underset{|}{N}}{-}O}$$

It is not unreasonable that oxygen transfers may proceed from such an adduct. The driving force for these reactions, we believe, derives from the enormous stability of the $PFe^{II}NO$ product.[27] These reactions also differ from those of other transition metal−nitro adducts[33] in that they require no metal or ligand activator (BF_3−Et_2O, Pd^{II}).

Experimental Section

General Methods. Argon (liquid carbonic) 99.998% was used throughout. *N*-Methylpyrrolidone (NMP) was passed through A-540 alumina to remove traces of peroxides, dried over sodium sulfate, and distilled under argon (bp 80−81 °C/10 mm). Chloroiron(III) octaethylporphyrin was prepared from the porphyrin in the manner previously described.[20] Potassium (18-crown-6) nitrite was obtained by refluxing potassium nitrite with 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) in methanol. Following concentration and crystallization, the white solid was recrystallized from benzene, dried, and stored in an evacuated desiccator over calcium sulfate. The white needles exhibited IR bands characteristic of NO_2^- (1269 cm^{-1}) and crown ether (CO at 1107 cm^{-1}). Carbon monoxide-13 (99% ^{13}C, Cambridge isotopes) showed only one ^{13}C resonance in the NMR at δ 183 and was used without purification. Nitric oxide (Matheson) was conveniently held for low-pressure storage by displacing water from an inverted 1 L separatory funnel that was fitted above the stopcock with a serum cap. This procedure removes any traces of $NO_2(N_2O_4)$ that may be present in the NO. Analysis of the gas, stored in this manner, by gas chromatography upon a 9 M−1/8 in. 8 Å molecular sieves column (30 °C, 30 mL/min He, thermal conductivity detector) showed only a trace of argon (syringe purge), 2.1 min, and NO, 5.7 min. The emergence times of other relevant gases under these conditions are as follows: N_2, 3.2 min; NO_2, 3.8 min; and N_2O > 30 min.

Dimethyl sulfide, propionaldelhyde, styrene, cyclohexene, and cyclohexenol were freshly distilled under argon. Triphenylphosphine (Aldrich) was used without purification. It showed only one ^{31}P resonance in the NMR at δ 8.0 corresponding to an authentic standard. Benzaldehyde, allyl chloride, cumene, tolueme, cyclohexen-3-ol, 1,5-hexadiene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, *cis*- and *trans*-1,2-dichloroethene, *cis*-stilbene, epichlorohydrin, and phenyl vinyl ketone were distilled under argon, and *trans*-stilbene was recrystallized before use. Vinyl chloride-*1,2*-^{13}C was prepared from 1,2-dichloroethane-*1,2*-^{13}C as previously described.[34] All substances were pure as judged by GC and NMR analysis.

Nitrite and nitrate analyses were conducted by the procedure of Chow and Johnstone.[35] A Hewlett-Packard 5989A mass spectrometer fitted with a 5980 gas chromatograph and data station was employed for GC−MS analyses. For inline GC−FT-IR−MS, a Hewlett-Packard 5965B FT-IR-unit was interposed between the GC exit and MS inlet or separate run spectrums for GC−IR and GC−MS were performed. ^{31}P, ^{1}H, and ^{13}C NMR analyses were acquired with a General Electric QE-300 spectrometer. Routine IR and UV−vis spectra were obtained with a Mattson 4020 Galaxy FT-IR and a Cary 118 °C UV−vis spectrophotometer, respectively.

Potassium crown ether (18-crown-6) ^{15}N-nitrite was prepared from K $^{15}NO_2^-$ (Cambridge Isotopes). The original salt (1.0 g) contained 5−10% of KNO_3. It was purified at great loss by dissolving in ice−water and concentrating the solution on a rotary evaporator for 3.5 min in a 50 °C bath. The white crystals were vacuum filtered and dried for 6 h in the rotary evaporator at 50 °C. The IR (KBr) showed a dominant intense nitrite band at 1240 cm^{-1}. A trace of nitrate (1352 cm^{-1}) was apparent, but it did not show in the ^{15}N-NMR (Figure 2). Reaction with 1,4,7,10,13,16-hexaoxacycloctdecane in methanol yielded the crown ether salt. Final recrystalization was from benzene. The ^{15}N-NMR of this salt is shown in Figure 2.

Nonreactive Substrates. The general procedure is illustrated with 2,3-dimethyl-2-butene. A 25 mL three-neck flask equipped with magnetic stirrer, argon inlet and outlet stopcocks, and a splayed set of two serum capped stopcocks fitted to the center neck was thoroughly purged with argon. The exit stopcock was connected to a mercury trap. Into the flask were placed 0.0125 g (2.0×10^{-5} mol) of ClFe(III)OEP, 0.090 g (2.6×10^{-5} mol) of K (18-crown-6) nitrite, 2 mL of NMP, and 0.04 mL of HOAc. The flask contents were stirred and purged with argon for 15 min. A 5 mL reactivial, fitted with serum cap, was charged with 2.2 mL of tetramethylethylene and purged vigorously with argon until the volume had diminished to 2.0 mL (15 min.). The olefin was then cannulated into the reaction vessel with hypodermic tubing. A separately purged 0.005 cm barrel-shaped spectrophotometric cuvette equipped with serum-capped argon inlet and outlet stopcocks was connected in line to the reaction mixture via the center neck, and gentle purging was continued until a few drops of sample were removed under argon pressure. (Note the face of the narrow cell fills readily with a small amount of liquid due to surface tension.) The visible spectrum corresponded to the starting iron(III) porphyrin at 2.5, 20, and 36 h. The sealed reaction mixture had been stirred and heated for 4 h at 72−74 °C before taking the 36 h sample. At this point an argon-purged solution of triphenylphosphine (0.05g, 1.8×10^{-4} mol) in 0.6 mL of NMP was transferred into the reaction. The spectrum of a subsequent sample indicated the beginning generation of the PFeNO adduct. Alternatively, unreactive substrates (No PFeNO in 36 h at room temperature) were allowed to react in the presence of the phosphine. In all cases the spectrum of the iron(II)−NO adduct fully developed overnight. Unreactive substrates established in this fashion are given in the text following Table 1.

Ozone Trapping Experiments. (a) With 2,3-Dimethyl-2-butene (Tetramethylethylene). A reaction exactly like that described above under nonreactive substrates was conducted in an atmosphere of pure oxygen. The iron(II)−NO adduct is not stable under these conditions, and it was not observed. At 16 h, the reaction flask was flushed with argon, and 0.4 g of powdered zinc and 0.5 mL of acetic acid were added. Stirring was continued for 3 h, whereupon the now red iron(II) porphyrin solution was opened to air and the flask

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contents were distilled through a short, small, minilab (vacuum) distillation head into an ice-cooled receiver fitted with a drying tube. The distillate was analyzed by gas chromatography on a 2-ft × 1/8 in. Porapak P column at 85 °C/30 mL/min He. A thermal conductivity detector was employed. Only two peaks were observed. They corresponded exactly to acetone (1.8 min) and tetramethylethylene TME (2.6 min). The yield of acetone assessed with an authentic standard of acetone in TME was 95 ± 5% (4.0×10^{-5} mol). Infrared spectra of the reaction distillate and standard run against TME were identical and showed a sharp carbonyl absorbtion at 1722 cm^{-1}. **(b) With 2-methyl-2-butene (Trimethylethylene).** The distillate of a reaction identical to the one above, except with 2-methyl 2-butene, was analyzed by GC on a 5 ft × 1/8 in. Porapak T column at 120 °C/40 mL/min He. Peaks corresponding to acetaldehyde (4.0 min), trimethylethylene (6−12 min, off scale), and acetone (14 min) were observed. Comparison with an authentic standard of acetaldehyde and acetone in 2-methyl-2-butene indicated the yields of acetone and acetaldehyde were 95 ± 5% and 90 ± 10%, respectively (2.0×10^{-5} mol each). Infrared spectra of the reaction distillate matched that of the standard. Though broadened, the two carbonyls were not resolved in these spectra (C=O at 1718 cm^{-1}, CHO, 2743 cm^{-1}). The combined yield of acetone and acetaldehyde estimated from carbonyl intensities was 90 ± 10%. GC−MS analyses of these reaction distillates was accomplished on a low load DB-5 column at −25 °C. For runs with 2-methyl-2-butene acetaldehyde was cleanly resolved (P, 44, P-H, 43, P-CHO, 15 and 29), but acetone tailed into the trimethylethylene peak. Nonetheless, it was clearly observable (P, 58, P-CH_3, 43). **(c) With Nitrite.** A stirred reaction mixture composed of 0.0125 g (2.0×10^{-5} mol) of ClFe(III)OEP, 0.018 g (5.2×10^{-5} mol) of K (18-crown-6) NO_2 in 4 mL of NMP, and 0.04 mL of HOAc was purged with oxygen for 3 min and sealed. After 16 h the solution was concentrated to dryness on the rotary evaporator at 45 °C initially at 20 mm and finally at 1 mm. The dried black concentrate was triturated with 4.0 mL of water and vacuum filtered. Two mL of this clear solution was analyzed for nitrite and nitrate by the procedure of Chow and Johnstone.[35] The recovery of nitrate and nitrite was 73%, and the ratio nitrate/nitrite was 0.5 ± 0.1 (theoretical 0.6). The remaining 2 mL were concentrated to dryness on the rotary evaporator and analyzed by IR (KBr). Strong bands for nitrate (1350 cm^{-1}), nitrite (1275 cm^{-1}),. and crown ether (1109 cm^{-1}) were present. A blank run without the porphyrin conducted and worked up in the same fashion generated no nitrate. In other blanks, under the conditions of a and b above, it was demonstrated the olefins are not oxidized by oxygen alone or by oxygen in the presence of iron porphyrin (no nitrite). Taken together with the lack of reactivity of these substrates under argon, it is established that porphyrin, oxygen, and nitrite are all essential for these reactions to occur.

Reactions. Typically, reactions were conducted in small flasks (25 mL or less) equipped with argon inlet and outlet stopcocks, a serum-capped stopcock, and a magnetic stirring bar. The argon outlet was connected to a mercury trap. Generally, for gaseous substrates, a solution of chloroiron(III) octaethylporphyrin (9.6×10^{-6} mol) and potassium (crown-ether) nitrite (3.84×10^{-5} mol) in 6 mL of NMP−1% HOAc was stirred and purged with argon for 0.5 h. Gaseous substrates were added via hypodermic syringe under argon. For liquid substrates 2 mL of substrate were separately purged before cannulating into 4 mL of NMP−1% HOAc containing the same amounts of porphyrin and nitrite salt indicated above. With the solid, triphenylphosphine, 2 mL of an 0.031 M solution in NMP was purged and transferred into the iron porphyrin/nitrite solution to begin the reaction. Thus, for most reactions $(PFe^{III}Cl)_o = 1.6 \times 10^{-3}$ M and (K(crown ether)NO2)$_o$ = 6.4×10^{-3} M.

All reactions were conducted at least three and usually five times.

NO to NO_2. (a) A reaction that yielded only qualitative results was initiated by the injection of 0.4 mL of NO gas into the above reaction mixture. Reaction proceeded immediately. A sample removed for spectral analysis exhibited the PFe^{II}-NO spectrum.[20] The reaction mixture and product gases were gently purged with argon into 2 mL of argon prepurged water. Analysis of this aqueous solution for nitrite and nitrate[11c] indicated both were produced, but the yield of nitrate never exceeded 2.4×10^{-6} mol (52%). Note: NO_2 (N_2O_4) hydrolyzes in water to NO_3^- and NO_2^{-3}. NO does not react with water, but in the presence of oxygen yields only NO_2^{-6}. (b) More quantitative runs were accomplished using thermal conductivity GC analysis on the column described above. For these reactions, a 20 mL reaction solution containing 2.0×10^{-5} mol of $PFe^{III}Cl$ and 2.6×10^{-5} mol of K (crown ether) nitrite in NMP 1% HOAc was treated with 2 mL of NO (8×10^{-5} mol). Two mL of the reaction mixture was transferred under argon via hypodermic tubing to a 2.5 mL barrel shaped cell with an 0.1 cm light path length. The cell was injected with 0.2 mL of NO. At 55 min, the reaction in the cell was 50% complete. GC analysis (above) of the cell gas phase showed argon NO_2 and NO. After 1 day, the reaction mixture was analyzed by GC. The spectrum was that of the $PFe^{II}NO$ adduct. For this purpose, a 250 μL gas-tight syringe was repeatedly flushed with argon, and following insertion into the gas phase of the reaction vessel was repeatedly filled and emptied into the gas phase. GC analysis showed both unreacted NO and NO_2 in the ratio of (NO/NO_2) 3.44. The ratio calculated from the amount of material charged is 6.2/1.8 = 3.48. That is, moles of NO_2 produced = mol of $PFe^{III} = {}^{18}/_{20}(2 \times 10^{-5}) = 1.8 \times 10^{-5}$. Moles of NO remaining is $8.0 \times 10^{-5} - 1.8 \times 10^{-5} = 6.2 \times 10^{-5}$.

CO to CO_2. A reaction mixture like that generally described above was flushed with 10 mL of ^{13}CO. The flask was shaken on a rotary shaker. After 1 day, the $PFe^{II}NO$ spectrum was observed and the reaction vessel was purged with argon into 2 mL of an argon purged 0.1 N NaOH solution. ^{13}C NMR analysis of the aqueous solution showed only a small amount of NMP and HOAc along with a large HCO_3^- signal at δ 167. The yield was quantitated by comparison with an $NaH^{13}CO_3$ standard spectrum obtained under identical conditions. A blank NMP−1% HOAc solution charged with ^{13}CO, but without porphyrin or nitrite salt treated in exactly the same manner, exhibited no $H^{13}CO_3^-$ in the NMR analysis.

Direct gas chromatographic analyses of the reactions of liquid substrates using flame ionization detection was accomplished with the columns indicated below. For GC−MS and GC−FT-IR−MS, the reaction mixture was first partially distilled at 20 mm into a cold trap (2-propanol−CO_2) to separate volatiles from NMP. The distillate was analyzed. For propionic acid, the distillate was treated with trimethylsilyl chloride and hexamethyldisilazane (Pierce-Trisil Conc.) 0.7 mL, and after the mixture was allowed to sit overnight, 50 μL of methanol was added before GC−MS analyses. For all analyses authentic standards were employed for quantitation and mass spectral analyses. Mass spectra and IR spectra of products were identical to authentic samples. Yields of products are reported in Table 1.

30 M GSQ capillary column, at 165°/40 mL/min He: dimethyl sulfide (1.2 min), dimethyl sulfoxide (20 min); at 100°/40 mL/min He followed by a temperature ramp at 8 min of 30°/min to 190°: cyclohexene (8.0 min), cyclohexenol (15 min), cyclohexenone (16.5 min).

30 M, RSL-150 capillary column, at 60°/4 mL/min He: propionaldyde (1.0 min), acetic acid (2.5 min), propionic acid (4.0 min); at 20°/4 mL/min He 2°/min temperature ramp trimethylsilyl propionate (15 min); at 60°/5 mL/min He: styrene (1.5 min), phenylacetaldehyde (5.0 min), styrene oxide (5.7 min). For GC−FT-IR−MS, a 30 M DB 5 column was employed at 60°/5 mL/min followed by a temperature ramp to 230 °C. Styrene oxide and phenylacetaldehyde emerged at 26.1 and 24 min, respectively.

Separate GC analysis of pure styrene oxide always showed some phenylacetaldehyde upon chromatography (5% or less). When the solution of styrene oxide in NMP−1% HOAc was allowed to stand for 2 days, it exhibited a 40% conversion to phenylacetaldehyde. A reaction with cyclohexenol yielded cyclohexenone quantitatively. This reaction is faster than the conversion of cyclohexene to cyclohexenone.

Triphenylphosphine and triphenylphosphine oxide were analyzed by ^{31}P NMR as indicated previously indicated.[20a]

Allyl Chloride. The red PFeNO reaction mixture was distilled after 36 h to bp 70 °C. Acrolein was quantitated in the distillate on a 30 m GSQ capillary column, yield 1.06×10^{-6} (112%). The mass spectrum of the 4.7 min peak matched exactly that of an authentic standard (P, 56, PH, 55, PCHO, 27). Upon standing under argon (without workup) this reaction slowly returned to the original spectrum of $PFe^{III}Cl$ (see kinetics). We presume this oxidation is the result of the slower reaction of excess allyl chloride with $PFe^{(II)}$ derived from the slow dissociating PFeNO adduct.[33] This would allow for some additional $PFeNO_2$ generation and additional oxidation, thus accounting for the consistently greater than 100% yields of product in this case. Note: epichlorohydrin (not detected) was not converted to acrolein under reaction conditions.

Allylbenzene. After 36 h, the reaction mixture was distilled at 110 °C/20 mm. *trans*-Cinnamaldehyde was quantitated from the distillate on a 30 m RSL-150 column, yield 4.8×10^{-6} mol (100%). The 11.1 min peak showed a MS and IR spectrum identical with authentic aldehyde. IR: CO,1710, C═C, 1624, CHO, 2735, 2805 cm^{-1}. MS: P, 132, PH (dominant) 131, PCHO, 103.

Benzaldehyde. After 36 h, the reaction mixture was treated with 80 μL of trisil concentrate. Excess reagent was decomposed with methanol, and the reaction mixture was distilled at 50−80 °C/7 mm. Trimethylsilyl benzoate was quantitated on the RSL-150 column, yield 9.6×10^{-6} mol (100%). A sample of the entire reaction mixture was subjected to GC−MS analysis prior to derivitization. The 19 min peak corresponded exactly to benzoic acid (P, 122, POH, 105, PCO_2H, 77).

Cumene. After 36 h, the reaction mixture was distilled at 110 °C/20 mm cumyl alcohol was quantitated on the RSL-150 column, yield, 9.6×10^{-5} mol (100%). The mass spectrum of the 30 min peak corresponded exactly to a standard, (P, 136, PCH_3, 121).

Toluene. For GC−MS analysis the reaction was distilled at 36 h. The MS of the 31 min peak on the RSL-150 column corresponded to authentic benzyl alcohol (P, 108, POH, 91, PCH_2OH, 77). For quantitation, a reaction at 36 h was treated with 80 μL of trisil concentrate and, after 10 min, with 0.5 mL of methanol. The mixture was then distilled to bp 110 °C/20 mm. Benzyl trimethylsilyl ether was quantitated on the RSL-150 column. The 5 min peak (30 °C/10 mL/min He) coincided with a sample of authentic ether, yield, 9.6×10^{-6} mol (100%).

***cis*-Stilbene.** Two mL of a 1.87 M solution of olefin in benzene was added under argon to 4 mL of NMP−1% HOAc containing the porphyrin and nitrite salt. After 36 h, the reaction was distilled. The fraction boiling at 90−110 °C/10 mm was analyzed on the RSL-150 column (70−220 °C/10 mL/min He). The 15 min peak comerged with *cis*-stilbene oxide and had a mass spectrum identical with an authentic standard (P, 196, PO, 180). In particular, no *trans*-stilbene oxide (17 min) was detected. The *trans*-olefin is inert.

1,5-Hexadiene. After 36 h, the reaction mixture was distilled at 130 °C. Analysis on the RSL-150 column showed a product peak at 8.5 min, the mass spectrum of which corresponded to *cis*- or *trans*-$CH_2{=}CHCH_2CH{=}CHCH_2OH$ (P, PCH_2OH, i.e., 98, 67). This structure is unconfirmed.

Kinetics. For kinetic analysis small-scale reactions were conducted in 0.1 or 1.0 cm cuvettes fitted with a serum-capped stopcock. NO, and the previously reported triphenylphosphine reaction, were examined at room temperature. However, the much slower reacting hydrocarbons and aldehydes were studied at 50 °C. For this purpose, initial solutions of iron porphyrin and nitrite salt were prepared and thoroughly purged with argon at room temperature. Spectra were recorded before and after the addition of nitrite. A shift in the λ_{max} of the iron(III) band from 627 to 619 nm was attendant upon the addition of nitrite, but there was no significant change in the spectrum upon warming the cuvette to 50 °C. Cells were thermostated at 50 °C, and reaction was initiated by injection of substrate. For initial slope analysis, each reactant was varied by a factor of at least 10. This established the general rate law. Typical concentrations were in the range $(PFe^{III})_o$ $12-4 \times 10^{-4}$ M , $(NO_2^-)_o$ 0.01−1 M, $(substrate)_o$ 0.01−1 M for pseudo-first-order runs. At least three runs were made with each substrate. The reproducibility run to run was ± 20%.

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