

Iron(II)-Induced Activation of Hydroperoxides for the Dehydrogenation and Monooxygenation of Organic Substrates in Acetonitrile

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Abstract: Solutions of $\text{Fe}^{\text{II}}(\text{MeCN})_4(\text{ClO}_4)_2$ in dry acetonitrile (MeCN) catalyze the rapid disproportionation of H_2O_2 to O_2 and H_2O , but all of the catalyst remains in the Fe(II) oxidation state. In the presence of organic substrates such as 1,4-cyclohexadiene, 1,2-diphenylhydrazine, catechols, and thiols, the Fe(II)- H_2O_2 /MeCN system yields dehydrogenated products (PhH, PhN=NPh, quinones, and RSSR) with conversion efficiencies that range from 100% to 17%. Although the Fe(II) catalyst does not promote the disproportionation of Me_3COOH or $m\text{-ClC}_6\text{H}_4\text{C}(\text{O})\text{OOH}$, these hydroperoxides are activated for the dehydrogenation of organic substrates. With substrates such as alcohols, aldehydes, methylstyrene, thioethers, sulfoxides, and phosphines, the $\text{Fe}^{\text{II}}(\text{H}_2\text{O}_2)^{2+}$ adduct promotes their monooxygenation to aldehydes, carboxylic acids, epoxide, sulfoxides, sulfones, and phosphine oxides, respectively: $\text{Fe}(\text{II}) + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{\text{II}}(\text{H}_2\text{O}_2)^{2+} + \text{RH} \rightarrow \text{Fe}(\text{II}) + \text{ROH} + \text{H}_2\text{O}$. The reaction efficiencies for the group of substrates with the Fe(II) adducts that are formed by H_2O_2 , Me_3COOH , and $m\text{-ClC}_6\text{H}_4\text{C}(\text{O})\text{OOH}$ have been evaluated. Also, the reaction rates for the substrate- $[\text{Fe}^{\text{II}}(\text{H}_2\text{O}_2)^{2+}]$ dehydrogenations and monooxygenations relative to that for Ph_2SO have been determined, as have the substituent effects for the monooxygenation of 4- $\text{XC}_6\text{H}_4\text{CH}_2\text{OH}$ and 4- $\text{XC}_6\text{H}_4\text{CH}(\text{O})$. The $\text{Fe}^{\text{II}}(\text{H}_2\text{O}_2)^{2+}$ adduct is an efficient catalyst for the autooxygenation of $\text{PhCH}(\text{O})$ to $\text{PhC}(\text{O})\text{OOH}$. Mechanisms are proposed for the Fe(II)-induced activation of hydroperoxides for the dehydrogenation and monooxygenation of organic substrates.

A recent Communication¹ described the iron(II)-induced activation of hydrogen peroxide in dry acetonitrile for the efficient dehydrogenation and monooxygenation of organic substrates. This chemistry is unique in that the $\text{Fe}^{\text{II}}(\text{MeCN})_4(\text{ClO}_4)_2$ catalyst rapidly disproportionates H_2O_2 in the absence of substrate but remains in the Fe(II) state (as it does for all of the substrate reactions). Also, the products from the Fe(II)- H_2O_2 /substrate reactions in dry MeCN are totally free of those associated with $\cdot\text{OH}$ -radical chemistry and the Fenton process.²⁻⁴ Although $\text{Me}_2\text{C}(\text{O})$ is unreactive, $\text{MeCH}(\text{O})$ is monooxygenated, and Me_2SO yields Me_2SO_2 exclusively (with $\cdot\text{OH}$ it yields CH_4 , C_2H_6 , and MeOH via production of methyl radicals).⁴ The reason for the total absence of any $\cdot\text{OH}$ -radical chemistry and of any Fe(III) in the product solutions is that the Fe(III)/Fe(II) redox couple in dry MeCN is +1.6 V vs. NHE, rather than +0.4 V (H_2O at pH 7).¹ This makes H_2O_2 an inadequate one-electron oxidant for Fe(II) in dry MeCN.

The present study has been directed to a detailed evaluation of the stoichiometries, kinetics, and product distributions for the iron(II)-induced dehydrogenations and monooxygenations for an extensive group of model substrates. The relative efficiencies for these processes when H_2O_2 , Me_3COOH , and $m\text{-ClC}_6\text{H}_4\text{C}(\text{O})\text{OOH}$ are used as oxidants and oxygenases have been determined, as have the effects of substrate substituents on their reaction rates. These results provide insight into the nature of the $\text{Fe}^{\text{II}}(\text{H}_2\text{O}_2)^{2+}$ reactive intermediate and a basis for the development of reasonable reaction mechanisms for the dehydrogenation and monooxygenation processes.

Experimental Section

Equipment. The reaction products were separated and identified with a Hewlett-Packard Model 5880 gas chromatograph that was equipped with a 12.5-m glass capillary column and by mass spectrometry (VG Industries ZAB reverse-geometry double-sector system with a GC sample inlet). UV-vis measurements were made with a Cary Model 219 spectrophotometer.

Chemicals and Reagents. Burdick and Jackson "Distilled in Glass" acetonitrile (<0.004% H_2O) was dried further by passing it through a column of Woelm N Super I alumina. The anhydrous $\text{Fe}^{\text{II}}(\text{MeCN})_4(\text{ClO}_4)_2$ salt was prepared by repeated recrystallization of $\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$ (reagent grade, G. Frederick Smith Chemical Co.) from dry MeCN. Pure H_2O_2 (assay >98%)⁵ was prepared from 30% H_2O_2 (J. T.

Baker). Careful removal of water from 10 mL of 30% H_2O_2 at 0 °C under high vacuum gave 2.5–3 mL of pure hydrogen peroxide. This was quickly dissolved into dry acetonitrile (25 mL) to make an approximately 1 M solution. The resulting solution was assayed by permanganate titration⁶ (the presence of acetonitrile did not interfere with the titration). The acetonitrile solution of H_2O_2 was stable at 0 °C; its assay did not change over a period of 1 month. Other reagents and substrates were analytical grade or highest purity available and were used without further purification.

Hazard Warning! Pure H_2O_2 is an exceptional oxidant. Trace quantities of reduced transition-metal ions can initiate its violent decomposition and oxidation of organic materials. Exercise extreme care, use adequate safety protection, and work with small quantities during the course of its purification, storage, and use.

Methods. The studies of substrate reactivities with the hydroperoxide adducts (H_2O_2 , Me_3COOH , and $m\text{-ClC}_6\text{H}_4\text{C}(\text{O})\text{OOH}$) of $\text{Fe}^{\text{II}}(\text{MeCN})_4(\text{ClO}_4)_2$ made use of a 30-mL glass cell with 0.5–1.0 mmol of substrate (RH) and 0.1–1.0 mmol of $\text{Fe}^{\text{II}}(\text{MeCN})_4(\text{ClO}_4)_2$ in 10 mL of CH_3CN . (The concentrations, the reaction temperatures, and reaction times are given in the tables.) The solution was deaerated by bubbling with argon gas for 5 min prior to the slow addition of 0.5–1.0 mL of 1 M hydroperoxide in MeCN. The resulting product solution was poured into water saturated with NaCl and extracted with diethyl ether (10 mL). The ether layer was washed with NaCl-saturated water, dried with anhydrous Na_2SO_4 , and analyzed by GC. Unknown product species were identified by GC-MS and confirmed by reference samples. The quantity of the product was calculated from a standard curve for the authentic sample or by comparison of the peak area to that for a standard material in the solution (biphenyl). The aqueous layer was assayed for residual Fe^{II} , Fe^{III} , and H_2O_2 by permanganate titration⁶ or by colorimetry with 1,10-*o*-phenanthroline or thiocyanate.⁶ Within the time intervals of the experiments (5–15 min), the hydroperoxides did not react with MeCN or with the substrates in the absence of $\text{Fe}^{\text{II}}(\text{MeCN})_4(\text{ClO}_4)_2$.

Results

The slow addition of dilute H_2O_2 [pure H_2O_2 (98%) in dry acetonitrile (MeCN)] to a solution that contains iron(II) [$\text{Fe}^{\text{II}}(\text{MeCN})_4(\text{ClO}_4)_2$] and an organic substrate (RH) in dry MeCN

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Table I. Conversion Efficiencies for Fe(II)-ROOH [R = H, Me₃C, *m*-ClC₆H₄C(O)] Induced Dehydrogenations and Monooxygenations of Organic Substrates (RH) in Acetonitrile^a

substrate reaction	reaction efficiency, ^b %		
	H ₂ O ₂ ^c	Me ₃ COOH	<i>m</i> -ClC ₆ H ₄ C(O)OOH
A. Dehydrogenations			
H ₂ O ₂ → O ₂	100		
1,4- <i>c</i> -C ₆ H ₈ → PhH	59	100	53
1,3- <i>c</i> -C ₆ H ₈ → [PhH/(C ₆ H ₇) ₂]	86 [1/2]	89 [2/1]	41 [1/2.5]
PhNHNHPh → PhN=NPh	100	75	100
3,5-(<i>t</i> -Bu) ₂ -1,2-(OH) ₂ C ₆ H ₂ → 3,5-(<i>t</i> -Bu) ₂ - <i>o</i> -benzoquinone	100	70	90
2PhCH ₂ SH → PhCH ₂ SSCH ₂ Ph	34/2	32/2	10/2
2PhSH → PhSSPh	68/2	32/2	10/2
B. Monooxygenations			
<i>c</i> -C ₆ H ₁₁ OH → C ₆ H ₁₀ (O)	47	27	45
MeCH ₂ OH → MeCH(O)	70	20	10
PhCH ₂ OH → PhCH(O)	100	72	48
PhCH ₂ OCMe ₃ → PhCH(O) + Me ₃ COOH	30	70	60
MeCH(O) → MeC(O)OH	20	10	27
PhCH(O) → PhC(O)OH	28	9	28
PhCH=CHMe → $\overset{\text{O}}{\text{C}}\text{HPh}/[\text{PhCH(O)} + \text{MeCH(O)}]$	16 [1/3]	13 [1/4]	29 [9/1]
$\overset{\text{O}}{\text{C}}\text{HPh} \rightarrow$ dioxane (dimer) + [PhCH(O) + MeCH(O)]	80 [7/3]	80 [4/1]	85 [19/1]
PhCH ₃ → PhCH ₂ OH [+PhCH(O), CH ₃ Ph(OH)]	0.3	2	0
(<i>c</i> -C ₆ H ₁₁) ₂ S → (<i>c</i> -C ₆ H ₁₁) ₂ SO	35	0	15
Ph ₂ S → Ph ₂ SO	27	7	51
Ph ₂ SO → Ph ₂ SO ₂	100	1	71
Ph ₃ P → Ph ₃ PO	100	100	47

^aTo 1.0 mmol of substrate and 0.5 mmol of [Fe^{II}(MeCN)₄](ClO₄)₂ in 10 mL of MeCN was added slowly 0.5 mmol of hydroperoxide (1 M ROOH in MeCN). Reaction time and temperature: 23 °C for 5 min (1,4-*c*-C₆H₈, 1,3-*c*-C₆H₈, PhNHNHPh, PhCH₂SH, PhSH, *c*-C₆H₁₁OH, CH₃CH(O), PhCH(O), PhCH₃, Ph₂SO, and Ph₃P); 5 °C for 10 min (3,5-(*t*-Bu)₂-1,2-(OH)₂C₆H₂, C₂H₅OH, PhCH₂OH, PhCH₂OCMe₃, PhCH=CHMe, $\overset{\text{O}}{\text{C}}\text{HPh}$, (*c*-C₆H₁₁)₂S, and Ph₂S). ^b100% represents one substrate dehydrogenation or oxygenation per ROOH added to the reaction system. In the case of H₂O₂ all of it is consumed, either by oxygenation of substrate or by disproportionation to O₂ and H₂O. Starting material is recovered for those substrates that react with less than 100% efficiency. ^cThese numbers represent a crude measure of the relative extent of reaction for the adduct with substrate and H₂O₂.

(<0.004% H₂O) results in the dehydrogenation (oxidation) or monooxygenation of RH. The net reactions and the conversion efficiencies (moles of substrate per mole of H₂O₂) for 1:0.5:0.5 RH-Fe(II)-H₂O₂ combinations of several organic substrates are summarized in Table I. The results from studies with Me₃COOH and *m*-ClC₆H₄C(O)OOH as the oxidant in place of H₂O₂ also are included. In sharp contrast to aqueous Fe(II)-H₂O₂ radical chemistry, the products from the RH-Fe(II)-ROOH combination in dry acetonitrile are characteristic of oxidase (dehydrogenation) and monooxygenation reactions. The total absence of products from ·OH-radical chemistry and of any Fe(III) in the product solutions confirms that classical Fenton chemistry does not occur.¹

In the absence of substrate, the combination of Fe(II) and H₂O₂ in dry MeCN results in the latter's rapid disproportionation to O₂ and H₂O, but the Fe(II) remains unoxidized. Similar combinations of Fe(II) with Me₃COOH or *m*-ClC₆H₄C(O)OOH do not promote their rapid disproportionation but rather facilitate a slow hydrolysis process (ROOH + H₂O → ROH + H₂O₂, assayed for ROH).

Because all of the H₂O₂ is consumed in the experiments of Table I, the reaction efficiency for the Fe(II)-H₂O₂ system represents a crude measure of the relative rate of reaction for the adduct with substrate and H₂O₂.

The relative order of the reaction rates for the substrates of Table I has been determined via a series of competition experiments with equimolar amounts of RH and Ph₂SO. Hence, the extent of oxidative conversion of RH relative to Ph₂SO from the slow addition of dilute H₂O₂ (0.5 mmol) to an MeCN solution that contains 0.5 mmol of RH, 0.5 mmol of Ph₂SO, and 0.5 mmol of Fe(II) has been measured; the results are summarized in Table II as relative amounts reacted. The bond energies for the weakest R-H bond of the substrates also are tabulated.⁷

In general, the [Fe(II)-ROOH]-induced dehydrogenations and monooxygenations for the substrates in Table I exhibit a first-order

Table II. Relative Extent of Reaction for Fe^{II}(H₂O₂)²⁺-Induced Dehydrogenations and Monooxygenations of Organic Substrates (RH) in Acetonitrile^a

substrate reaction	relative amt reacted ^b (RH/Ph ₂ SO)	R-H bond energy, ^c kcal
A. Dehydrogenations		
1,4- <i>c</i> -C ₆ H ₈ → PhH	8.7	74
1,3- <i>c</i> -C ₆ H ₈ → PhH + (C ₆ H ₇) ₂	8.7	70
PhNHNHPh → PhN=NPh	5.4	
2PhCH ₂ SH → PhCH ₂ SSCH ₂ Ph	1.3 (2.6/2)	86
2PhSH → PhSSPh	2.2 (4.4/2)	83
B. Monooxygenations		
<i>c</i> -C ₆ H ₁₁ OH → C ₆ H ₁₀ (O)	0.12	95
MeCH ₂ OH → MeCH(O)	0.17	90
PhCH ₂ OH → PhCH(O)	0.27	80
PhCH ₂ OCMe ₃ → PhCH(O)	0.32	80
MeCH(O) → MeC(O)OH	0.48	85
PhCH(O) → PhC(O)OH	0.57	80
PhCH=CHMe → $\overset{\text{O}}{\text{C}}\text{HMe} + \text{PhCH(O)} + \text{MeCH(O)}$	0.54	
(<i>c</i> -C ₆ H ₁₁) ₂ S → (C ₆ H ₁₁) ₂ SO	0.55	
Ph ₂ S → Ph ₂ SO	0.26	
Ph ₂ SO → Ph ₂ SO ₂	1.00	
Ph ₃ P → Ph ₃ PO	16.1	

^aTo the acetonitrile solution (10 mL) of the substrates (0.5 mmol each) and [Fe^{II}(MeCN)₄](ClO₄)₂ (0.5 mmol) was slowly added 1 M H₂O₂ (0.5 mmol) under argon at 23 °C. The reaction mixture was stirred for 5 min. After the extraction with ether, the relative extent of conversion was determined on the basis of the residual substrates as determined by gas chromatography. ^bThe numbers represent the relative extent for the oxidative conversion from the addition of 0.5 mmol of H₂O₂ to 0.5 mmol of RH and 0.5 mmol of Ph₂SO in 10 mL of MeCN. ^cReference 7.

dependence on the RH and ROOH concentrations for their reaction efficiencies (and reaction rates). The results for another series of competitive reactions for the 4-XC₆H₄CH₂OH and 4-

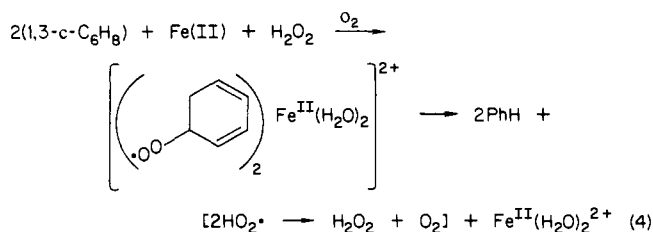
(7) "CRC Handbook of Chemistry and Physics", 61st ed.; CRC Press: Boca Raton, FL, 1980-1981; p F-235.

Table IV. Fe^{II}(H₂O₂)²⁺-Induced Autooxygenation of Organic Substrates in Acetonitrile^a

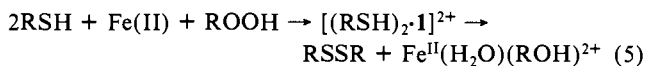
substrate reaction	conversion efficiency, ^b %	
	Ar (1 atm)	O ₂ (1 atm) ^c
A. Dehydrogenation		
1,4-c-C ₆ H ₈ → PhH	42 ± 5	59 ± 6
1,3-c-C ₆ H ₈ → [PhH + (C ₆ H ₇) ₂]	23 [83% PhH]	18 [100% PhH]
PhSH → PhSSPh	46/2	55
PhCH ₂ SH → PhCH ₂ SSCH ₂ Ph	54/2	20
B. Monoxygenation		
PhCH ₂ OH → PhCH(O)	8 (19) ^d	7 (13) ^d
PhCH(O) → PhC(O)OH	1	370 [100% Fe(III)]

^aTo a 10-mL acetonitrile solution that contained 1.0 mmol of substrate and 0.1 mmol of Fe^{II}(MeCN)₄(ClO₄)₂ was added slowly 0.1 mmol of H₂O₂ in 0.1 mL of acetonitrile at 23 °C. After the solution was stirred for 5 min, it was quenched, extracted with ether, and analyzed by gas chromatography. ^b100% represents one substrate dehydrogenation or oxygenation per H₂O₂ added to the system. ^cOxygen was bubbled through the solution during the reaction. ^dFor 0.2 mmol of Fe(II) and 0.2 mmol of H₂O₂.

Support for such a process is provided by the absence of any (C₆H₇)₂ dimer as a product when O₂ is present in the reaction matrix (Table IV). Thus, with O₂ present the initial formation of c-C₆H₇ in the reactive complex apparently is followed by a coupling to give c-C₆H₇OO·, which then dissociates to PhH and HO₂· (eq 4).⁸ This radical-radical coupling by ·O₂· precludes dimerization of the c-C₆H₇· radicals and results in benzene as the only product.



Although H₂S is oxygenated to H₂SO₄ by the Fe^{II}-H₂O₂ adduct (four H₂O₂ molecules per H₂S),¹ thiols (both aromatic and aliphatic) are dehydrogenated by the Fe^{II}(ROOH)²⁺ complex to give disulfides as the only product. The reaction stoichiometry of two RSH molecules per ROOH is the same as for the dimerization of 1,3-c-C₆H₈ (eq 3); a similar bisadduct for the reaction complex probably is formed (eq 5). Because the side-on configuration



(1, eq 1) of the Fe^{II}(ROOH)²⁺ adduct appears to be the reactive form, the lower yields for the *m*-ClC₆H₄C(O)OOH oxidant may indicate that the end-on configuration (2, eq 1) is dominant for the peracid. The chemistry of reaction 5 is equivalent to that of *glutathione peroxidase* (an enzyme that contains selenocysteine in its active site),⁹ and the Fe^{II}(ROOH)²⁺ complex may represent a reaction mimic for the enzyme.

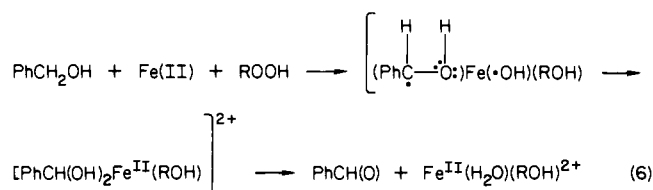
There is a rough inverse correlation between the relative reaction rates of Table II and the weakest R-H bond energy of the substrates. This is in accord with the biradical and homolytic bond-scission mechanisms that are proposed in eq 3-5.

Iron(II)-Induced Activation of Hydroperoxides for the Monoxygenations of Organic Substrates. The results of Table I establish that the Fe(II)-ROOH adducts in dry MeCN are effective monoxygenases for alcohols (and for activated olefins, thioethers, sulfoxides, and phosphines). The reaction rate for PhCH₂OH is about twice as fast as for MeCH₂OH (Table II), probably because the C-H bond energy of the methylene group of the former is 10

kcal lower. Also, the reaction rates for a given alcohol are in the order H₂O₂ > Me₃COOH > *m*-ClC₆H₄C(O)OOH (Table I), and the rate of oxygenation for PhCH₂OCMe₃ by the Fe^{II}(Me₃COOH)²⁺ adduct is essentially the same as that for PhCH₂OH (ratio of reactivity: PhCH₂OH/PhCH₂OCMe₃ = 1.0/1.2).

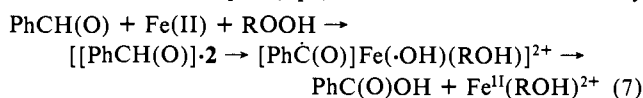
The data of Table III for *p*-XC₆H₄CH₂OH indicate that the substituent effect is greater by a factor of 7 for X = MeO over that for X = NO₂. This substituent effect is too small for a hydride-transfer mechanism (from the α-carbon) but is compatible with a radical-intermediate process with an initial H-atom transfer.

All of these results indicate that the Fe^{II}(ROOH)²⁺ adduct of eq 1 oxygenates alcohols (and ethers) and that H₂O₂ and Me₃COOH are more reactive than *m*-ClC₆H₄C(O)OOH. A mechanism that is consistent with these observations involves either (1) the homolytic scission of the side-on RO-OH bond [1, eq 1; induced by the bound substrate (ROH)] and the subsequent abstraction by RO· of a H atom from the α-carbon or (2) the direct abstraction by the oxene oxygen of the end-on configuration (2, eq 1) of a H atom from the α-carbon and the subsequent addition of the resulting ·OH group to the carbon radical (eq 6).



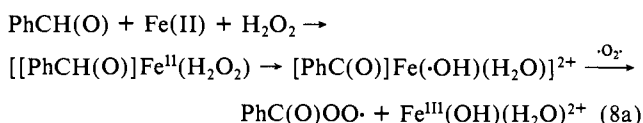
The resulting hemiacetal dissociates to give the aldehyde and H₂O [R'OH when the substrate is an ether (ROR')]. Because ethers are as reactive as alcohols and give the same aldehyde product, the process must be a monoxygenation to the hemiacetal rather than a dehydrogenation (concerted removal of hydrogen atoms from the α-carbon and the OH group).

Reference to the data of Tables I and II confirms that the Fe^{II}(ROOH)²⁺ activated complexes from H₂O₂, Me₃COOH, and *m*-ClC₆H₄C(O)OOH are effective monoxygenases for aldehydes. The substituent data of Table III for 4-XC₆H₄CH(O) also are compatible with a biradical mechanism. However, there is an inverse substituent effect to that for alcohols, and the much higher rates when H₂O₂ and *m*-ClC₆H₄C(O)OOH are the oxidants relative to those for Me₃COOH may indicate that the oxene character of the end-on configuration (2, eq 1) makes it the dominant reactive complex (eq 7). This same enhanced reactivity



for the H₂O₂ and *m*-ClC₆H₄C(O)OOH adducts of Fe(II) relative to that for Me₃COOH is observed for substrates that undergo an O-atom addition rather than a biradical process. Apparently, the Fe^{II}(Me₃COOH)²⁺ adduct has a limited tendency to take on significant oxene character in the end-on configuration (2, eq 1).

The dramatic enhancement by molecular oxygen of the rate and extent of the Fe^{II}(H₂O₂)²⁺-PhCH(O) reaction (Table IV) is indicative of an autooxygenation process. Thus, the formation of the reactive intermediate complex provides a biradical center than can couple with triplet oxygen (·O₂·) to give PhC(O)OO· in an initiation step (eq 8a). The coupling by ·O₂· with the carbon

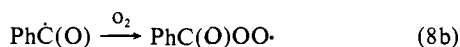
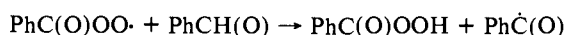


radical leaves an [Fe·OH] center, which goes to the observed Fe^{III}(OH)²⁺ product. The peroxy radical [PhC(O)OO·] from the initiation step apparently abstracts a H atom from a second PhCH(O) and the resulting PhC(O)· radical couples with another ·O₂· in the propagation step (eq 8b). The Fe(II)-catalyzed oxy-

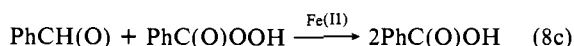
(8) Howard, J. A.; Ingold, K. V. *Can. J. Chem.* 1967, 45, 785.

(9) Nicholls, P. *Biochim. Biophys. Acta* 1972, 279, 306.

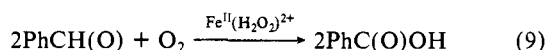
Propagation



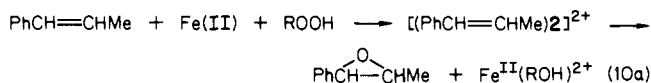
generation of another PhCH(O) by the peracid represents a second propagation step (eq 8c)



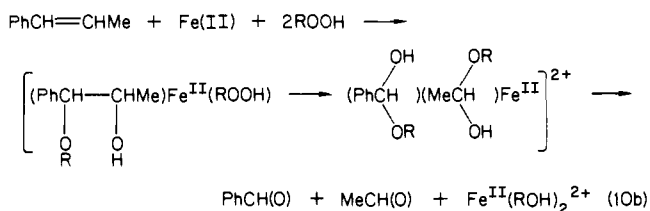
The sum of these processes is an $\text{Fe}^{\text{II}}(\text{H}_2\text{O}_2)^{2+}$ -catalyzed auto-oxygenation of PhCH(O) (eq 9)



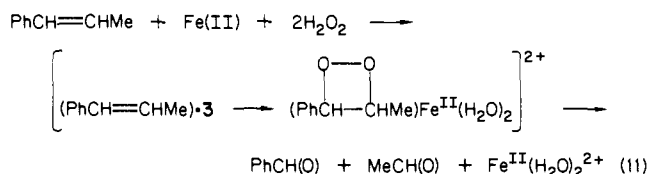
The monooxygenation of methylstyrene (PhCH=CHMe) to form the epoxide (Table I) appears to involve an O-atom transfer from the end-on configuration (2, eq 1) of the $\text{Fe}^{\text{II}}(\text{ROOH})^{2+}$ complex (eq 10a). However, a significant fraction of the products



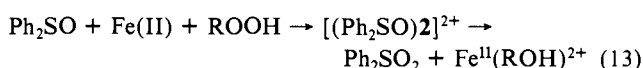
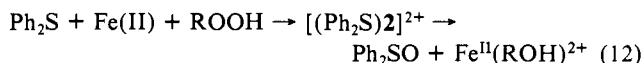
from this substrate (75% for H_2O_2 and 80% for Me_3COOH , Table I) is the result of a dioxygenation to give PhCH(O) and MeCH(O). When *m*-ClC₆H₄C(O)OOH is the oxidant, only 10% of the PhCH=CHMe that reacts is dioxygenated. These results are consistent with the proposition that the end-on configuration of the $\text{Fe(II)}-m\text{-ClC}_6\text{H}_4\text{C(O)OOH}$ adduct has the most oxene character and favors O-atom transfer to PhCH=CHMe and that the $\text{Fe(II)}-\text{H}_2\text{O}_2$ and $\text{Fe(II)}-\text{Me}_3\text{COOH}$ adducts react via a biradical mechanism. A reasonable mechanistic pathway that involves two ROOH molecules per PhCH=CHMe molecule is presented in eq 10b. The latter process is dominant when the



ROOH concentration is greater than that for the Fe(II) catalyst. When the oxidant is H_2O_2 and is in excess relative to Fe(II) and substrate, the disproportionation process of eq 2 is favored via an activated dioxygen intermediate (3, eq 2), which dioxygenates aromatic olefins [e.g., PhCH=CHPh \rightarrow 2PhCH(O)].¹ Hence, PhCH=CHMe probably is subject to dioxygenation by this activated intermediate [$\text{Fe}^{\text{II}}(\text{H}_2\text{O}_2)^{2+}$] (eq 11).



The limited activity of the $\text{Fe}^{\text{II}}(\text{Me}_3\text{COOH})^{2+}$ adduct with thioethers (R_2S) and sulfoxides (R_2SO) (Table I) probably results because it has the least oxene character. The simplest pathway to the monooxygenated products for these substrates is via O-atom transfer from the end-on complex (2, eq 1) with the bound sub-



strates inducing the heterolytic formation of a reactive oxygen atom from the bound (OOH(R)) group [R = H or *m*-ClC₆H₄C(O)]. Phosphines (e.g., Ph₃P) probably are monooxygenated by a mechanism analogous to that for Ph₂S (eq 12).

The formulations of eq 1 and 2 for the reactive forms of the $\text{Fe(II)}-\text{ROOH}$ adducts represent unique electrophilic centers that are consistent with reasonable monooxygenase (1 and 2) and dioxygenase (3) reaction mechanisms. The monooxygenase formulations (1 and 2, eq 1) also are consistent with the redox stoichiometry of the cytochrome P-450 cycle¹⁰ and represent a form of oxygen activation that promotes electrophilic abstraction of a hydrogen atom (or O-atom transfer) to give radical (or oxene) activated intermediates¹¹ and the monooxygenation of cytochrome P-450 substrates (Table I).

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Registry No. $\text{Fe}^{\text{II}}(\text{MeCN})_4(\text{ClO}_4)_2$, 97690-72-7; H_2O_2 , 7722-84-1; Me_3COOH , 75-91-2; *m*-ClC₆H₄CO₂H, 937-14-4; 1,4-c-C₆H₈, 628-41-1; 1,3-c-C₆H₈, 592-57-4; PhNHNHPh, 122-66-7; 3,5-(*t*-Bu)₂-1,2-(OH)₂C₆H₂, 1020-31-1; PhCH₂SH, 100-53-8; PhSH, 108-98-5; C₆H₁₁-OH, 108-93-0; MeCH₂OH, 64-17-5; PhCH₂OH, 100-51-6; PhCH₂OCMe₃, 3459-80-1; MeCH(O), 75-07-0; PhCH(O), 100-52-7; PhCH=CHMe, 637-50-3; PhCHOCHMe, 20697-03-4; PhCH₃, 108-88-3; (c-C₆H₁₁)₂S, 7133-46-2; Ph₂S, 139-66-2; Ph₂SO, 945-51-7; Ph₃P, 603-35-0; *p*-MeOC₆H₄CH₂OH, 105-13-5; *p*-MeC₆H₄CH₂OH, 589-18-4; *p*-ClC₆H₄CH₂OH, 873-76-7; *p*-FC₆H₄CH₂OH, 459-56-3; *p*-O₂NC₆H₄CH₂OH, 619-73-8; *p*-MeOC₆H₄CHO, 123-11-5; *p*-MeC₆H₄CHO, 104-87-0; *p*-FC₆H₄CHO, 459-57-4; *p*-O₂NC₆H₄CHO, 555-16-8.

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