Epoxidation Reactions

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Mononuclear Nonheme Iron(III)-Iodosylarene and High-Valent Iron-Oxo Complexes in Olefin Epoxidation Reactions

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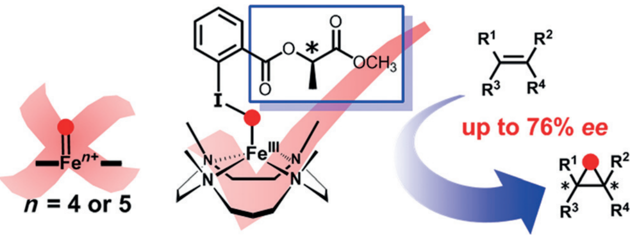
Abstract: *High-spin iron(III)-iodosylarene complexes are highly reactive in the epoxidation of olefins, in which epoxides are formed as the major products with high stereospecificity and enantioselectivity. The reactivity of the iron(III)-iodosylarene intermediates is much greater than that of the corresponding iron(IV)-oxo complex in these reactions. The iron(III)-iodosylarene species—not high-valent iron(IV)-oxo and iron(V)-oxo species—are also shown to be the active oxidants in catalytic olefin epoxidation reactions. The present results are discussed in light of the long-standing controversy on the one oxidant versus multiple oxidants hypothesis in oxidation reactions.*

Elucidation of the nature of reactive intermediates in dioxygen activation and oxidation reactions by metalloenzymes and their model compounds is the subject of current research in the biological, bioinorganic, and oxidation chemistry communities.[1–3] In the enzymatic and biomimetic reactions, high-valent metal-oxo species have been widely accepted as reactive intermediates, and their reactivities and reaction mechanisms have been well-established in various oxidation reactions. However, there has been an intriguing, long-standing controversy on the involvement of multiple oxidizing species in catalytic oxidation reactions.[4–6] The controversy stems from the observations that products formed in the catalytic oxidation reactions by heme enzymes and iron porphyrin models are different depending on the reaction conditions (e.g. site-directed mutagenesis and radical clock experiments in cytochromes P450 and porphyrin, and axial ligand effects in iron porphyrin reactions).[5,6] However, experimental and theoretical studies dispute the multiple oxidants hypothesis on the basis of the observation that iron(III)-hydroperoxo complexes are sluggish oxidants and high-valent iron-oxo porphyrin complexes can exhibit diverse reactivity patterns under different circumstances.[7,8]

Recently, a number of metal-oxygen intermediates, including mononuclear nonheme iron(IV)-oxo and iron(III)-oxygen species, were successfully synthesized and characterized spectroscopically and/or structurally.[3,9] Thus, it is timely to investigate the reactivities of those isolated metal-oxygen complexes and the mechanisms of oxidation reactions under stoichiometric conditions. Furthermore, by comparing the reactivities of the metal-oxygen species, the long-standing controversy on the one oxidant versus multiple oxidants hypothesis may be resolved in metal-catalyzed oxidation reactions.

One of the often-discussed oxidation reactions in the one oxidant versus multiple oxidants debate is the epoxidation of olefins by iodosylbenzene (PhIO) catalyzed by metal complexes.[6,10] In the catalytic reactions, epoxidizing intermediates were mainly proposed on the basis of product analysis. Furthermore, the epoxidation reactions were rarely investigated using in situ generated metal-iodosylbenzene complexes under stoichiometric conditions and a comparison of the reactivity of iron-iodosylbenzene and iron-oxo complexes in the epoxidation reactions has not previously been performed. We therefore decided to investigate the epoxidation of olefins with spectroscopically well-characterized iron(III)-iodosylarene complexes, such as $[(13\text{-TMC})\text{Fe}^{\text{III}}\text{-OIPh}]^{3+}$ (**1**; 13-TMC = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotridecane)[11] and its analogues prepared with pentafluoroiodosylbenzene {F_5PhIO; $[(13\text{-TMC})\text{Fe}^{\text{III}}\text{-OIPhF}_5]^{3+}$ (**2**)}, iodosylmesitylene {MesIO; $[(13\text{-TMC})\text{Fe}^{\text{III}}\text{-OIMes}]^{3+}$ (**3**)}, soluble iodosylbenzene {^{s}PhIO; $[(13\text{-TMC})\text{Fe}^{\text{III}}\text{-OIPh}^{s}]^{3+}$ (**4**)}, and chiral iodosylbenzene {^{c}PhIO; $[(13\text{-TMC})\text{Fe}^{\text{III}}\text{-OIPh}^{c}]^{3+}$ (**5**)} (see Table S1 in the Supporting Information for the structures of the iodosylarenes used in this study). We now report for the first time that iron(III)-iodosylarene complexes are highly reactive in the epoxidation of olefins; epoxides are formed as the major product with high stereospecificity and enantioselectivity. The iron(III)-iodosylarene complexes are much more reactive than the corresponding iron(IV)-oxo complex, $[(13\text{-TMC})\text{Fe}^{\text{IV}}(\text{O})]^{2+}$ (**6**),[12] in the epoxidation of olefins. We also report that the iron(III)-iodosylarene adducts, not high-valent iron(IV)- and iron(V)-oxo complexes, are the active oxidants in the catalytic olefin epoxidation reactions (Scheme 1).

Iron(III)-iodosylarene (**1–5**) and iron(IV)-oxo (**6**) complexes bearing a common supporting ligand (13-TMC) were



Scheme 1. Proposed intermediates—high-valent iron(IV)- and iron(V)-oxo and iron(III)-iodosylarene complexes—in olefin epoxidation reactions.

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synthesized (see the Experimental Section in the Supporting Information for detailed reaction procedures and Figures S1–S4 for spectroscopic characterization), and their reactivities were investigated in the epoxidation of olefins under identical conditions. The addition of styrene to solutions of iron(III)-iodosylarene adducts **1**–**5** in a solvent mixture of acetone and CF_3CH_2OH (v/v = 3:1) at −60 °C resulted in the disappearance of the intermediates with a first-order decay profile (Figure 1 a for the reaction of **1**; see Figure S5 for the reactions of **2**–**5**). The first order rate constants, determined by pseudo-first-order fitting of the kinetic data for the decay of the iron(III)-iodosylarene adducts, increased linearly with the increase of the styrene concentration (Figure 1 b; see Figure S6), thus leading us to determine second-order rate constants for the reactions of **1**–**5** (see Table S1). A kinetic isotope effect (KIE) value of 1.0(1) was also obtained in the oxidation of styrene and [D_8]styrene by **1** (Figure 1 b), thereby indicating that the oxidation of styrene by **1** occurs by an oxygen atom transfer (OAT) mechanism. Furthermore, the activation parameters for the epoxidation of styrene and deuterated [D_8]styrene by **1** were found to be 7.2 kcal mol^{-1} for $\Delta H^{\neq}$ and −27 cal mol^{-1} K^{-1} for $\Delta S^{\neq}$ in both reactions (see Figure S7). A ρ value of −1.3 was obtained from the Hammett plot of $\log k_2$ against σ_p^+ (see Table S2 and Figure S8) for the epoxidation of *para*-X-substituted styrenes (X = Me, H, Cl, and NO_2) and *meta*-chlorostyrene by **1**. This result indicates an electrophilic character of the iron(III)-iodosylarene adducts in the olefin epoxidation reactions, as frequently observed in high-valent iron(IV)-oxo porphyrin π-cation radicals and nonheme iron(IV)-oxo complexes.[7b,13] Other aromatic olefins having different oxidation potentials were used as substrates in the epoxidation of olefins by **1**, and second-order rate constants were determined for these reactions (see Table S2 and Figure S9). When the second-order rate constants were plotted against the oxidation potentials (E_{ox}) of substrates, a good linear correlation was observed with a slope of −2.2 (Figure 1 c), as observed in the epoxidation of olefins by high-valent metal-oxo complexes in heme systems (e.g. iron(IV)-oxo porphyrin π-cation radical).[14] In contrast to the iron(III)-iodosylarene complexes, $[(13\text{-TMC})Fe^{IV}(O)]^{2+}$ (**6**) did not react with any of the aromatic olefins (e.g. styrene) under the identical reaction conditions, thus demonstrating that the iron(III)-iodosylarene adducts are much more reactive than the corresponding iron(IV)-oxo complex in the olefin epoxidation reactions.

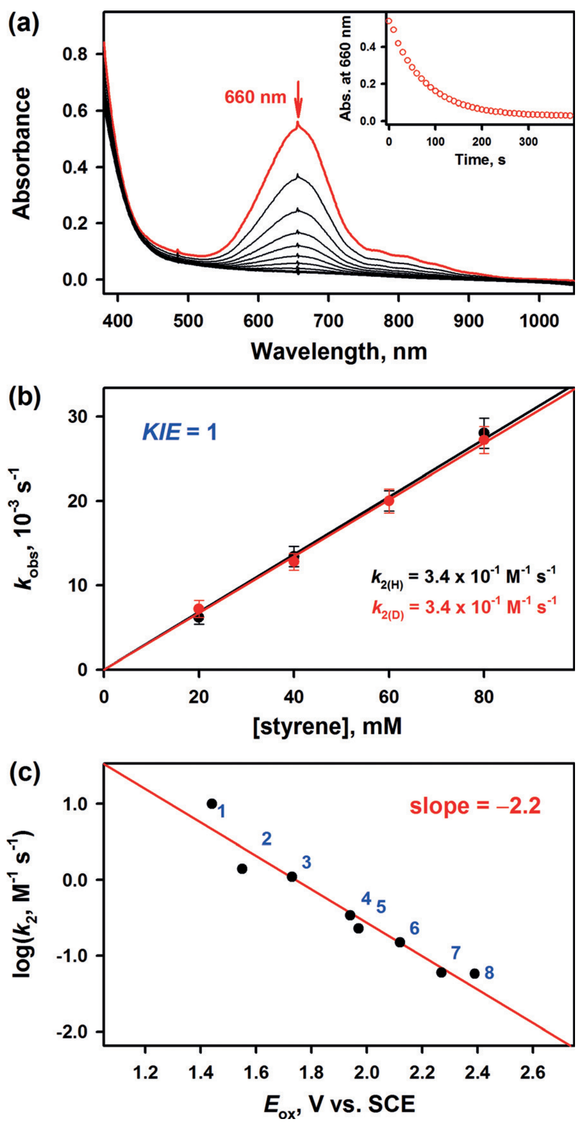
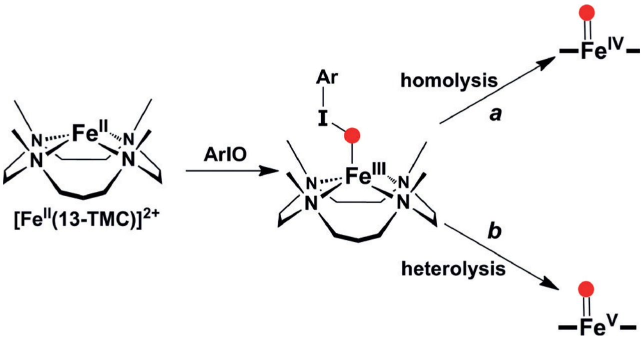


Figure 1. a) UV/Vis spectral changes observed in the reaction of **1** (1.0 mM) and styrene (20 mM) in the presence of $HClO_4$ (1.2 equiv) in acetone/CF_3CH_2OH (3:1) at −60 °C. The inset shows the time course monitored at 660 nm. b) Plots of pseudo-first-order rate constants (k_{obs}) against the concentrations of styrene (black circles) and [D_8]styrene (red circles) to determine second-order rate constants (k_2) for the oxidation of these substrates by **1** in the presence of $HClO_4$ (1.2 equiv) in acetone/CF_3CH_2OH (3:1) at −60 °C. c) Plot of log k_2 against the E_{ox} values of stilbenes and styrene derivatives (see Table S2) for the reactions of **1** with stilbenes and styrene derivatives [*trans*-stilbene (1), *cis*-stilbene (2), 4-methylstyrene (3), styrene (4), 4-chlorostyrene (5), 3-chlorostyrene (6), 2,6-dichlorostyrene (7), and 4-nitrostyrene (8)].

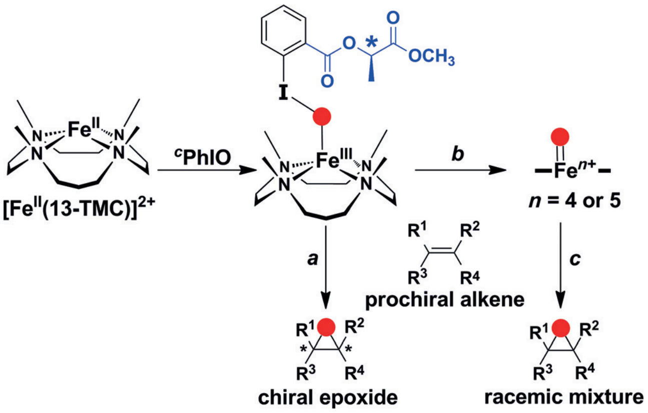
Product analysis of the reaction solution of the styrene epoxidation by iron(III)-iodosylarene complexes revealed the formation of styrene oxide as the major product together with a small amount of 2-phenylacetaldehyde (see Table S1). In addition, based on an ^{18}O-labeling experiment performed with [^{18}O]-**1** (75(5) % ^{18}O),[11] the oxygen atom in the epoxide product (77(4) % ^{18}O) was found to derive from the iodosylbenzene group in **1** (see Figure S10). Similarly, the epoxidation of styrene derivatives by **1** afforded predominantly epoxide products (see Table S3). In addition, the epoxidation reaction was highly stereospecific; the epoxidation of *cis*- and *trans*-stilbenes by **1** afforded *cis*- and *trans*-stilbene oxides, respectively, without giving isomerized products (see Table S4, entries 4 and 5). In the competitive epoxidation of *cis*-stilbene versus *trans*-stilbene, *trans*-stilbene oxide was formed predominantly, which is consistent with the kinetic data obtained in the stoichiometric kinetic studies (see Tables S2 and S4, entry 6). Finally, we found that an iron(II) species was formed as the major decayed product of **1** in the olefin epoxidation reactions (see Figure S11).

The reactivities of the iron(III)-iodosylarene and iron(IV)-oxo complexes were also investigated in the epoxidation of aliphatic olefins, such as cyclooctene, cyclohexene, norbornene, and 1-octene. As we had observed in the epoxidation of aromatic olefins, **1** disappeared rapidly upon addition of the aliphatic olefins at a low temperature (e.g. −60 °C), even in the reaction with a less reactive olefin (i.e. 1-octene; see spectral changes in Figure S12). Second-order rate constants were determined by plotting first-order rates against the concentrations of the aliphatic olefins (see Figure S13). When the second-order rate constants were plotted against the oxidation potentials (E_{ox}) of the aliphatic olefins, a good linear correlation was observed (see Table S5 and Figure S14). Furthermore, product analysis revealed that epoxides were formed as the major product (e.g. cyclooctene oxide with a yield of 81(5) %; see Table S4). Furthermore, in the reaction of cyclohexene, cyclohexene oxide (66(5) %) was obtained as the major product along with the formation of cyclohex-2-enol (21(2) %) and cyclohex-2-enone (3.0(2) %; see Table S4). The source of the oxygen atom in the cyclohexene oxide product (71(5) % ^{18}O) was found to be the iodosylbenzene group in **1** on the basis of an ^{18}O-labeling experiment performed with [^{18}O]-**1** (75(5) % ^{18}O; see Figure S15).[11] It is of interest to note that the preference of the C=C epoxidation over the allylic C−H bond activation in the oxidation of cyclohexene by the iron(III)-iodosylbenzene adduct (**1**) is different from that reported in the oxidation of cyclohexene by mononuclear nonheme iron(IV)-oxo complexes.[15] In the latter reactions, allylic oxidation products, such as cyclohex-2-enol, were formed predominantly with a trace amount of cyclohexene oxide. In addition, a KIE value of 1.0(1) was obtained for the oxidation of cyclohexene and [D$_{10}$]cyclohexene by **1** (see Figure S13c); it is worth noting that high KIE values (ca. 60) were obtained in the oxidation of cyclohexene by the nonheme iron(IV)-oxo complexes [(N4Py)Fe^{IV}(O)]$^{2+}$ and [(Bn-TPEN)Fe^{IV}(O)]$^{2+}$ (N4Py = *N*,*N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine and Bn-TPEN = *N*-benzyl-*N*,*N*′,*N*′-tris(2-pyridylmethyl)ethane-1,2-diamine).[15a] Finally, [(13-TMC)Fe^{IV}(O)]$^{2+}$ (**6**) did not react with cyclohexene under the identical reaction conditions.

We then carried out the epoxidation of olefins by the iron(II) complex [(13-TMC)Fe^{II}]$^{2+}$ and PhIO at low (e.g. −60 °C) and room temperatures under the catalytic reaction conditions (e.g. [(13-TMC)Fe^{II}]$^{2+}$ (1.0×10^{-3} M), substrate (2.0×10^{-1} M), and PhIO (3.0×10^{-2} M); see the Experimental Section in the Supporting Information for detailed reaction procedures). In all of the reactions, epoxides were obtained as major products (see Table S4). Moreover, the product distributions were the same as those observed in the stoichiometric reactions performed with in situ generated iron(III)-iodosylbenzene adducts (see Table S4), thereby leading us to propose that the active oxidant that effects the olefin epoxidation in the catalytic reactions is iron(III)-iodosylarene adducts. Furthermore, we rule out the involvement of an iron(IV)-oxo species, which is formed by a homolytic O−I bond cleavage of the iron(III)-iodosylarene adducts (Scheme 2, pathway *a*), as a reactive species in the catalytic epoxidation reactions, since we have shown in the stoichiometric kinetic studies that the iron(IV)-oxo intermediate does not react with olefins (see above). However, we cannot rule out the possibility that an iron(V)-oxo species is formed by heterolytic cleavage of an O−I bond of the iron(III)-iodosylarene adducts (Scheme 2, pathway *b*) and this intermediate is involved as a reactive species in the catalytic epoxidation reactions. Indeed, high-valent iron(V)-oxo species have been frequently proposed as active oxidants in various oxidation reactions by nonheme iron catalysts.[16] Since we failed to synthesize the proposed iron(V)-oxo intermediate bearing the 13-TMC ligand, we synthesized an iron(III)-iodosylarene complex with a chiral iodosylarene, [(13-TMC)Fe^{III}-OIPh^{c}]$^{3+}$ (**5**), and used it in the olefin epoxidation, on the assumption that if this intermediate is involved in the olefin epoxidation, we would observe the formation of epoxides with a high enantiomeric excess (Scheme 3, pathway *a*). If an iron(V)-oxo complex is involved in the olefin epoxidation, then we would observe the formation of a racemic mixture (Scheme 3, pathways *b* and *c*).



Scheme 2.



Scheme 3.

The iodosylarene (^{c}PhIO) with a chiral auxiliary on the benzene ring was synthesized from an optically active hypervalent iodine reagent (see the structure in Scheme 3; see also Table S1).[17] The reaction of [(13-TMC)Fe^{II}]$^{2+}$ with ^{c}PhIO in acetone/CF$_3$CH$_2$OH (3:1) at −60 °C afforded a high-spin iron(III)-iodosylarene complex, [(13-TMC)Fe^{III}-OIPh^{c}]$^{3+}$ (**5**; see Figures S2–S4). Interestingly, the reaction of **5** with chalcone afforded chalcone oxide as the major product with a good enantioselectivity (i.e. ca. 76 % *ee*; see Table 1, entry 1 and Figure S16). Similarly, moderate enantiomeric excess (*ee*) values were obtained in the epoxidation of trisubstituted aromatic α,β-enones, such as 2-(4-methylbenzylidene)-1-tet-

Table 1: Stoichiometric and catalytic oxidation of olefins by a chiral iron(III)-iodosylarene adduct (**5**).[a]

Entry	Substrate	Yield [%][b]	*ee* [%][b]	Configuration
1	chalcone	36	76	(2*R*,3*S*)
2	2-(4-methylbenzylidene)-1-tetralone	42	67	(2*R*,3*S*)
3	2-(4-chlorobenzylidene)-1-tetralone	38	53	(2*S*,3*R*)

[a] Reaction conditions: $[(13\text{-TMC})\text{Fe}^{\text{III}}\text{-OIPh}^{c}]^{3+}$ (1.0 mM), $HClO_4$ (1.2 mM), olefin (20 mM), acetone/CF_3CH_2OH (3:1), −60 °C, 10 min. All reactions were performed under an Ar atmosphere. See the Supporting Information for detailed information, including HPLC spectrum (see Figure S16). [b] Yields and *ee* values were determined by HPLC on a chiral stationary phase.

ralone and 2-(4-chlorobenzylidene)-1-tetralone (Table 1, entries 2 and 3). These results demonstrate unambiguously that the intermediate responsible for the epoxidation of olefins should contain a chiral center (i.e. **5**) and that the high-valent iron(IV)- and iron(V)-oxo complexes, which do not possess a chiral center, are not the reactive species in the olefin epoxidation. Furthermore, when we carried out the catalytic olefin epoxidation using the chiral iodosylarene (^{c}PhIO), epoxides were produced predominantly with virtually the same *ee* values as obtained in the stoichiometric reactions (see Figure S16). These results lead us to conclude that the catalytic epoxidation of olefins by the nonheme iron complex and iodosylarenes is mediated by the iron(III)-iodosylarene species (Scheme 3, pathway *a*), not the iron(V)-oxo species (Scheme 3, pathway *c*).

In summary, we have reported that nonheme iron(III)-iodosylarene complexes are highly reactive in the epoxidation of olefins; epoxides are formed as the major product with high stereospecificity and enantioselectivity. We have also demonstrated that the iron(III)-iodosylarene species are the active oxidants in the catalytic epoxidation of olefins by iodosylarenes. The current results provide strong evidence that can resolve the long-standing controversy on the one oxidant versus multiple oxidants hypothesis in the catalytic epoxidation of olefins by metal complexes and iodosylarenes.

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Keywords: bioinorganic chemistry · enzyme models · epoxidation · iron complexes · reaction mechanisms

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