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Enzyme Models

Highly Reactive Nonheme Iron(III) Iodosylarene Complexes in Alkane Hydroxylation and Sulfoxidation Reactions**

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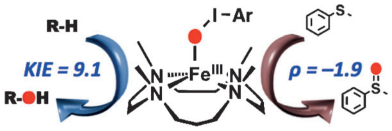
Abstract: *High-spin iron(III) iodosylarene complexes bearing an N-methylated cyclam ligand are synthesized and characterized using various spectroscopic methods. The nonheme high-spin iron(III) iodosylarene intermediates are highly reactive oxidants capable of activating strong C–H bonds of alkanes; the reactivity of the iron(III) iodosylarene intermediates is much greater than that of the corresponding iron(IV) oxo complex. The electrophilic character of the iron(III) iodosylarene complexes is demonstrated in sulfoxidation reactions.*

High-valent iron oxo species, such as iron(IV) oxo porphyrin π-cation radicals and nonheme iron(IV) oxo complexes, have been invoked as key intermediates in a variety of biological oxidation reactions, including alkane hydroxylation and sulfoxidation.[1] A large number of iron(IV) oxo complexes have been synthesized and investigated in the oxidation reactions as chemical models of heme and nonheme iron enzymes.[2] It has been demonstrated that high-valent iron oxo species are indeed strong oxidants capable of activating C–H bonds of unactivated hydrocarbons.

Very recently, nonheme iron(III) superoxo and high-spin iron(III) hydroperoxo complexes have been proposed or demonstrated as active oxidants in C–H bond activation reactions, although the intermediates are able to activate only weak C–H bonds in hydrocarbons.[3,4] Other metal–oxidant adducts (M^{n+}–OX; for example, X = IAr, OH, OR, halides) have also been synthesized and characterized spectroscopically and/or structurally, and their reactivities have been investigated in oxygen-atom transfer (OAT) reactions, such as epoxidation and sulfoxidation. For example, Fujii and coworkers reported that iron(III)–OCl porphyrin and manganese(IV) iodosylarene salen complexes are competent oxidants in OAT reactions.[5] McKenzie and Lennartson reported a crystal structure of a nonheme iron(III) iodosylbenzene complex and used it in a sulfoxidation reaction.[6] Lei and coworkers reported spectroscopic evidence for a manganese iodosylarene porphyrin adduct.[7]

Over the past two decades, there has been continuing interest in oxidation reactions in which multiple oxidants are involved.[8,9] In most cases, the multiple oxidant hypothesis has been proposed based on product analysis using mechanistic probes (e.g., radical-clock experiments and competitive epoxidation of *cis*- vs. *trans*-alkenes).[9] In contrast to OAT reactions, the involvement of metal–oxidant adducts has not been proposed in the hydroxylation of alkanes with strong C–H bonds. To our knowledge, no kinetic studies have been conducted on the proposed metal–oxidant species (M^{n+}–OX) in oxidation reactions. Herein, we report the synthesis and characterization of high-spin iron(III) iodosylarene complexes bearing an N-methylated cyclam ligand (proposed structure given in Scheme 1). The coordination of iodosylarene to the iron(III) center is evidenced spectroscopically and



Scheme 1. Proposed structure of high-spin iron(III) iodosylarene complexes bearing an N-methylated cyclam ligand and reactions investigated in this work. Filled red circle = ^{18}O.

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by conducting experiments with ^{18}O-labeled water. The iron(III) iodosylarene intermediates are highly reactive oxidants capable of activating strong C–H bonds (e.g. cyclohexane; Scheme 1). The electrophilic character of the iron(III) iodosylarene adducts is also demonstrated in sulfoxidation reactions (Scheme 1).

The reactions of [Fe^{II}(13-TMC)(CF$_3$SO$_3$)$_2$] (**1**, 13-TMC = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotridecane)[10] with iodosylarenes, such as iodosylbenzene (PhIO) or pentafluoroiodosylbenzene (F$_5$PhIO), in a solvent mixture of acetone and CF$_3$CH$_2$OH (3:1) at −40 °C resulted in the formation of blue intermediates. These intermediates, denoted **2** (from the reaction with PhIO) and **3** (from the reaction with F$_5$PhIO), respectively, have maximum UV/Vis absorption bands at $\lambda = 660$ nm (Supporting Information, Figure S1). The intermediates were highly unstable and decayed to an iron(IV) oxo complex, [Fe^{IV}(O)(13-TMC)]$^{2+}$ (**4**), with a half-life ($t_{1/2}$) of approximately 20 s (Figures S1 and S2). Interestingly, when the same reactions were carried out in the presence of 1.2 equivalents of HClO$_4$, the stability of the intermediates increased markedly ($t_{1/2} \approx 300$ s; Figure 1 a for **2**; also see Figure S3a for **3**). Thus, we were able to characterize intermediates **2** and **3** with various spectroscopic methods, including coldspray ionization time-of-flight mass spectrometry (CSI-TOF MS), UV/Vis absorption, electron paramagnetic resonance (EPR), Mössbauer, and resonance Raman (rRaman) spectroscopies.

The UV/Vis absorption spectra of **2** and **3** exhibit an absorption band at $\lambda = 660$ nm (Figure 1 a for **2**; Figure S3 for **3**). The CSI-TOF MS of **2** exhibits a prominent ion peak at m/z 766.1 (Figure 1 b; Figure S4 for full mass spectrum of **2**), whose mass and isotope distribution patterns correspond to [Fe(OIPh)(13-TMC)(CF$_3$CH$_2$O)(CF$_3$SO$_3$)]$^+$ (calculated m/z 766.1). When **2** was prepared with ^{18}O-labeled PhI^{18}O, a mass shift from m/z 766.1 to 768.1 was observed (Figure 1 b, inset), indicating that **2** contains an oxygen atom. The CSI-TOF MS of **3** was also taken and analyzed similarly (Figure S5). The rRaman spectra of **2** and **3**, obtained upon $\lambda = 441.6$ nm excitation in CF$_3$CH$_2$OH at −40 °C, show isotopically sensitive bands at 783 and 772 cm^{-1}, respectively (Figure 1 c for **2**; Figure S6 for **3**). The peaks were shifted to 751 and 740 cm^{-1} when the intermediates **2** and **3** were prepared with PhI^{18}O and F$_5$PhI^{18}O, respectively. The observed shift from the ^{16}O to ^{18}O samples of $\Delta = 32$ cm^{-1} is in good agreement with the calculated value of 39 cm^{-1} expected for a diatomic O–I oscillator.[11] The rRaman spectrum of the decayed product, [Fe^{IV}(O)(13-TMC)]$^{2+}$ (**4**), shows one isotopically sensitive band at 833 cm^{-1}.[10]

The X-band EPR spectra of **2** and **3**, recorded in a frozen acetone/CF$_3$CH$_2$OH (3:1) solution at 5 K, show signals that are characteristic of $S = 5/2$ Fe^{III} (Figure S7).[12] The Mössbauer spectrum of **2**, recorded at 4.2 K (Figure S8), in the absence of a strong applied magnetic field displays a doublet typical of iron(IV) oxo species ($\delta = 0.12\ \mathrm{mm\,s^{-1}}$, $\Delta E_Q = 1.98\ \mathrm{mm\,s^{-1}}$)[2e,f,10b] and two doublets corresponding to Fe(III) centers ($\delta = 0.43\ \mathrm{mm\,s^{-1}}$, $\Delta E_Q = -1.02\ \mathrm{mm\,s^{-1}}$ and $\delta = 0.36\ \mathrm{mm\,s^{-1}}$, $\Delta E_Q = -0.60\ \mathrm{mm\,s^{-1}}$). The spectrum also displays diffuse absorption spreading over a large velocity domain. To characterize this absorption, spectra were recorded in variable applied magnetic fields (Figure 1 d). A spin Hamiltonian fit allowed simulation of this absorption as an $S = 5/2$ Fe^{III} complex[10b] accounting for approximately 30 % of total iron, with $\delta = 0.37\ \mathrm{mm\,s^{-1}}$ and $\Delta E_Q = -0.59\ \mathrm{mm\,s^{-1}}$ (Table S1 for complete parameters), that was assigned to **2**. The Fe(III) centers giving rise to the doublets were confirmed to have an

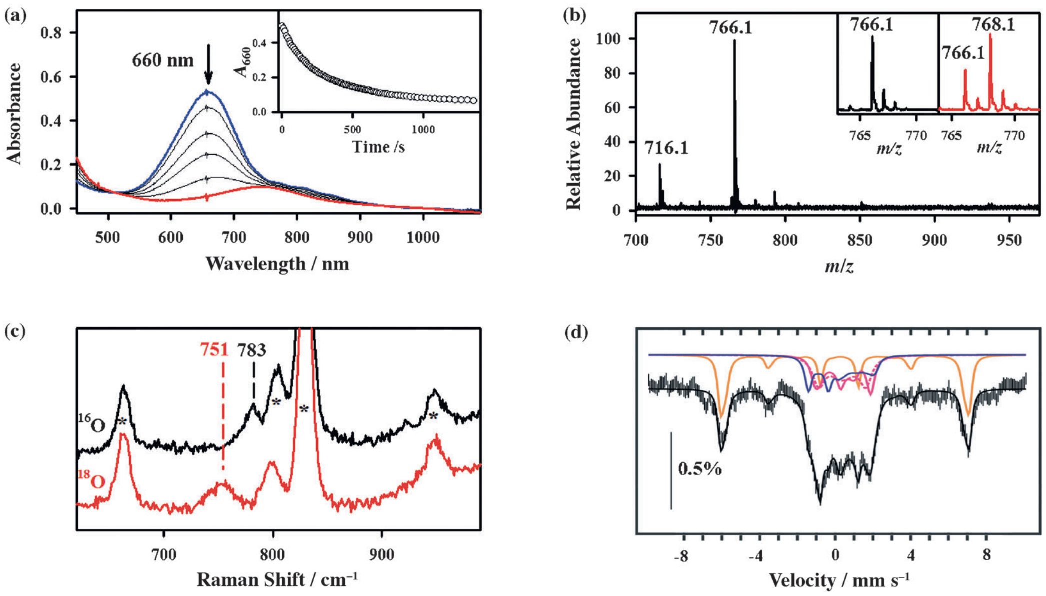


Figure 1. a) UV/Vis absorption spectral changes of **2** formed from the reaction of [Fe(13-TMC)(CF$_3$SO$_3$)$_2$] (1.0 mM) with PhIO (3.0 equiv) in the presence of HClO$_4$ (1.2 equiv) in acetone/CF$_3$CH$_2$OH (3:1) at −40 °C. Compound **2**, with a maximum absorption band at $\lambda = 660$ nm, was generated within 20 s. Inset: change in absorption intensity, monitoring at $\lambda = 660$ nm, with respect to time, for the natural decay of **2**. b) CSI-TOF MS spectrum of **2** in the presence of HClO$_4$ (1.2 equiv) in acetone/CF$_3$CH$_2$OH (3:1) at −50 °C. Black plots: CSI-TOF MS of **2** prepared using PhI^{16}O. Red plot: CSI-TOF MS of **2** prepared using PhI^{18}O. c) rRaman spectra of [Fe^{III}(^{16}OIPh)(13-TMC)]$^{3+}$ (4.0 mM, black line) and [Fe^{III}(^{18}OIPh)(13-TMC)]$^{3+}$ (4.0 mM, red line) upon $\lambda = 441.6$ nm excitation in CF$_3$CH$_2$OH at −40 °C. The peaks marked with an asterisk are ascribed to solvent. d) Mössbauer spectrum of **2** recorded at 4.2 K in a 7 T parallel applied magnetic field (vertical bars). The solid black line is the theoretical spectrum generated by adding individual spin-Hamiltonian simulations (colored lines). Components are assigned to **2** (orange), an Fe^{IV} product converted from **2** (blue), and an Fe^{III} dinuclear complex (pink).

$S = 0$ ground state and were assigned to a μ-oxo dimer. Based on the spectroscopic characterization of **2** and **3**, it can be concluded that high-spin iron(III) iodosylarene complexes, assigned as $[Fe^{III}(OIPh)(13\text{-TMC})]^{3+}$ for **2** and $[Fe^{III}(OIPhF_5)(13\text{-TMC})]^{3+}$ for **3**, were produced in the reactions of **1** with iodosylarenes.

The coordination of iodosylarene in **2** and **3** was further confirmed by carrying out an isotopically ^{18}O-labeled water experiment. This experiment was based on the previous report that metal–iodosylarene adducts exchange the oxygen atom (e.g. M^{n+}-O-IAr) with labeled water, $H_2{}^{18}O$.[5c,13] Compounds **2** and **3** were firstly prepared with $PhI^{16}O$ and $F_5PhI^{16}O$, respectively, and then a small amount of $H_2{}^{18}O$ was added to these reaction solutions. Although the UV/Vis spectra of **2** and **3** remained intact, the CSI-TOF MS of the resulting solutions showed that approximately 70% of the oxygen atoms in **2** and **3** exchanged with $H_2{}^{18}O$ within 30 s (Figure S9 and S10). This result provides the first direct evidence that iron(III) iodosylarene complexes exchange their oxygen atom with $H_2{}^{18}O$ at a fast rate [see Eq. (1)].[14]

$$[(13\text{-TMC})Fe^{III}\text{-}^{16}O\text{-IAr}]^{3+} + H_2{}^{18}O \rightleftharpoons [(13\text{-TMC})Fe^{III}\text{-}^{18}O\text{-IAr}]^{3+} + H_2{}^{16}O \qquad (1)$$

The reactivities of the iron(III)–iodosylarene adducts, **2** and **3**, were investigated in the C–H bond activation of hydrocarbons at −40 °C. Upon addition of cumene to a solution of **2**, the intermediate was converted into a new species (**5**) which gives rise to an isosbestic point at $\lambda = 537$ nm (Figure 2a). First-order rate constants, determined by the pseudo-first-order fitting of the kinetic data for the decay of **2** (Figure 2a, inset), increased linearly with increasing cumene concentration, giving rise to a second-order rate constant of $2.1 \times 10^{-1}\,\text{M}^{-1}\,s^{-1}$ at −40 °C. A kinetic isotope effect (KIE) of 9.1(5) was obtained for the oxidation of cumene by **2** (Figure 2b). In the case of **3**, a second-order rate constant of $1.4 \times 10^{-1}\,\text{M}^{-1}\,s^{-1}$ with a KIE of 13(2) was determined for the oxidation of cumene at −40 °C (Figure S11). This result suggests that the reactivity of **2** is slightly greater than that of **3**. We also determined second-order rate constants for the oxidation of other substrates by **2** (Table S2 and Figure S12), showing a linear correlation between the reaction rates and the C–H bond dissociation energy (BDE) of substrates (Figure 2c). Under identical reaction conditions, **4** did not react with cumene, indicating that the reactivity of the iron(III)–iodosylarene adducts is much greater than that of the corresponding iron(IV) oxo species. On the basis of the large KIE value and the good correlation between reaction rates and BDEs of substrates, we conclude that the C–H bond activation of substrates by the iron(III)–iodosylarene adducts is the rate-determining step.

Analysis of the products obtained from the reaction mixtures revealed the formation of alcohols as a major product in the oxidation of alkanes by **2** and **3** (Table S3). For example, the oxidation of cumene by **2** under an inert atmosphere yielded 2-phenylpropan-2-ol (20%), α-methylstyrene (21%), and acetophenone (3%). When the cumene oxidation was performed with approximately 70% of ^{18}O-labeled **2** (**2**-^{18}O), approximately 67% of ^{18}O was found in the 2-phenylpropan-2-ol product (Figure S13). The high ratio of alcohol to ketone products obtained and the incorporation of ^{18}O into the products demonstrates that the products are derived from the metal-mediated oxidation reaction, not from an autooxidation reaction. We also analyzed **5**, a decomposition product of **2** in the oxidation of cumene, using ESI-MS and EPR and assigned **5** as an iron(III) species (Experimental Section and Figures S14 and S15).

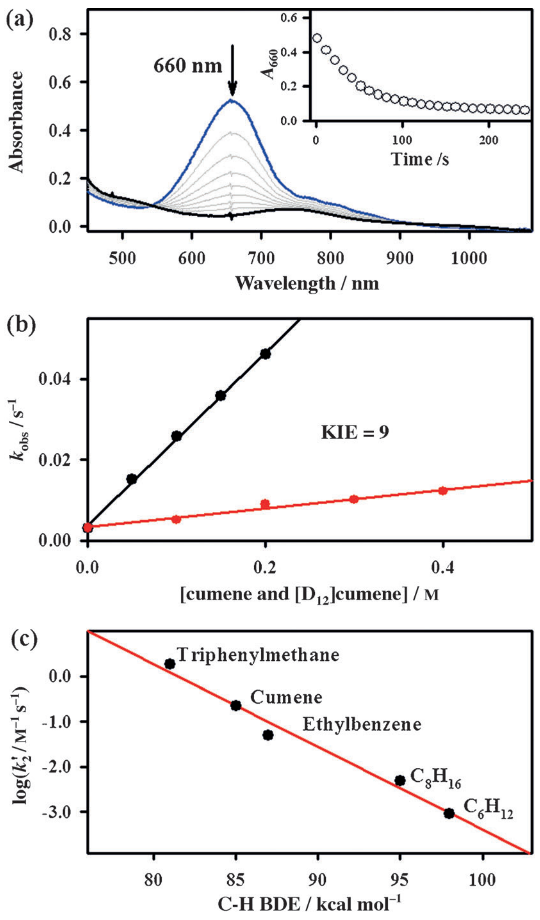


Figure 2. a) UV/Vis absorption spectral changes observed in the reaction of **2** (1.0 mM) with cumene (100 equiv) in the presence of $HClO_4$ (1.2 equiv) in acetone/CF_3CH_2OH (3:1) at −40 °C. Inset: change in absorption intensity of **5**, monitoring at $\lambda = 660$ nm, with respect to time. b) Plots of pseudo-first-order rate constants (k_{obs}) against the concentration of cumene (black circles) or [D$_{12}$]cumene (red circles) to determine second-order rate constants (k_2) in the oxidation reaction of cumene or [D$_{12}$]cumene by **2**. Reaction carried out in the presence of $HClO_4$ (1.2 equiv) in acetone/CF_3CH_2OH (3:1) at −40 °C. c) Plot of $\log k_2'$ against the C–H BDE of substrates for the reactions of **2**. Second-order rate constants, k_2, were determined and then adjusted for reaction stoichiometry to yield k_2' based on the number of target C–H bonds within substrates (see data in Table S2 and Figure S12).

The reactivities of **2** and **3** were also investigated in sulfoxidation reactions. Upon addition of 10 equivalents of thioanisole, **2** and **3** disappeared within 0.2 s with a first-order decay profile (Figure 3a for **2**; Figure S16 for **3**). The pseudo-first-order rate constants increased proportionally with the concentration of thioanisole to afford second-order rate constants of $k_2 = 3.5 \times 10^3$ and $2.7 \times 10^3\,\text{M}^{-1}\,s^{-1}$ at −60 °C for **2**

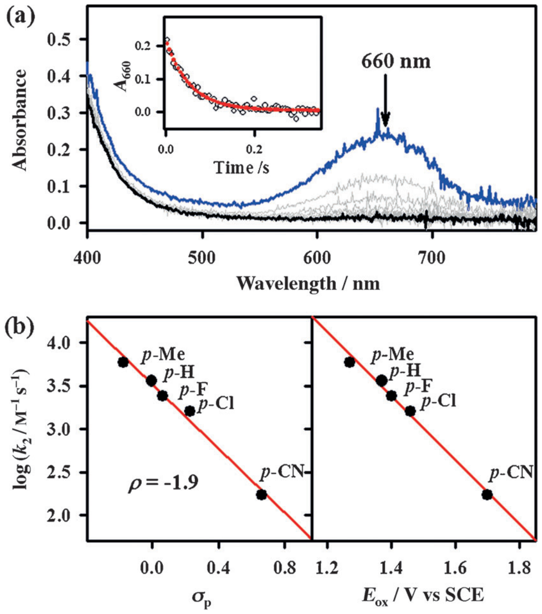
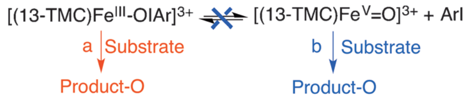


Figure 3. a) UV/Vis absorption spectral changes observed in the reaction of **2** (0.50 mM) with thioanisole (10 equiv) in the presence of $HClO_4$ (1.2 equiv) in acetone/CF_3CH_2OH (3:1) at −60 °C. Inset: change in absorption intensity, monitoring at λ = 660 nm, with respect to time. b) Plot of $\log k_2$ against the σ_p values (left) and E_{ox} (right) of *para*-substituted thioanisoles for the reactions of **2**.

and **3**, respectively (Figure S17). The reactivity of **2** is slightly greater than that of **3**, as observed in the alkane hydroxylation reactions. To investigate the electronic effect of *para*-substituents on the oxidation of thioanisoles by iron(III)–iodosylarene adducts, **2** was treated with *para*-substituted thioanisoles, *para*-X-$PhSCH_3$ (X = Me, H, F, Cl, and CN). A Hammett plot of the second-order rate constants versus σ_p of substrates gave a ρ value of −1.9 (Figure 3b, left; Table S4). Such a negative ρ value illustrates the electrophilic character of the iron(III)–iodosylarene adducts in OAT reactions, as frequently observed in the sulfoxidation of thioanisoles by high-valent metal oxo, metal superoxo, and metal hydroperoxo complexes of heme and nonheme ligands.[15,16] In addition, we observed a good linear correlation when the rates were plotted against oxidation potentials (E_{ox}) of thioanisoles (Figure 3b, right). The negative slope of −3.7 indicates that the oxidation of sulfides by iron(III)–iodosylarene adducts proceeds by a direct oxygen-atom transfer mechanism.[15,16] The product analysis of the reaction solution of the oxidation of thioanisole by **2** revealed that methyl phenyl sulfoxide was produced with a high yield (> 90% based on the amount of **2** used). The source of oxygen in the sulfoxide product was found to be the iodosylarene group of **2**, on the basis of an ^{18}O-labeling experiment performed with **2**-^{18}O (see Experimental Section for reaction conditions and Figure S18). In contrast to the alkane hydroxylation reaction, **2** was not converted into an iron(III) species (such as **5**) but to an iron(II) complex (Figure S19).

Finally, we conducted the alkane hydroxylation and sulfoxidation reactions with the iron(III)–iodosylarene adducts **2** and **3** in the presence of an excess amount of F_5PhI. In iron porphyrin systems, an equilibrium exists between an iron(IV) oxo porphyrin π-cation radical complex and an iron(III) iodosylarene porphyrin complex in the presence of iodoarene and it is the iron(IV) center which is the reactive species in olefin epoxidation reactions.[17] If there is an equilibrium between an iron(III)–iodosylarene adduct and an iron(V) oxo species, which is formed by O−I bond cleavage of the iron(III)–iodosylarene adduct, the presence of an excess amount of iodoarene should decrease the reaction rate (see Scheme 2). Compound **3** was employed in the cumene hydroxylation and thioanisole oxidation reactions in the presence of F_5PhI (50 equiv). It was found that the reaction rates were the same as those obtained in the reactions carried out in the absence of F_5PhI (Figure S20). These results demonstrate unambiguously that the iron(III)–iodosylarene adduct (Scheme 2, pathway a), not the iron(V) oxo complex (Scheme 2, pathway b), is the reactive species for the hydroxylation and sulfoxidation reactions.



Scheme 2. See text for details.

In summary, we have reported the synthesis, characterization, and reactivity of nonheme iron(III) iodosylarene complexes. The intermediates are highly reactive in both alkane hydroxylation and sulfoxidation reactions. Based on the results of the mechanistic studies and product analysis, we were able to conclude that the iron(III)–iodosylarene adducts are the reactive species responsible for the oxidation reactions. These results provide an example of metal–oxidant adducts which can transfer their oxygen atom to organic substrates prior to the conversion into metal oxo species.[8]

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[14] We cannot exclude the possibility that the oxygen exchange between iron(III) iodosylarene complexes and $H_2^{18}O$ may occur after the iodosylarene in the iron(III) iodosylarene complexes dissociates first and exchanges with $H_2^{18}O$. Then, the ^{18}O-labeled iodosylarenes are rebound to an iron(III) species to give the ^{18}O-labeled iron(III) iodosylarene complexes.

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