

Catalytic Alkyl Hydroperoxide and Acyl Hydroperoxide **Disproportionation by a Nonheme Iron Complex**

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Supporting Information

ABSTRACT: Alkyl hydroperoxides are commonly used as terminal oxidants because they are generally acknowledged to be stable toward disproportionation compared with H₂O₂. We show that alkylperoxide disproportionation is effectively catalyzed by the $[Fe(tpena)]^{2+1}$ (tpena = N,N,N'-tris(2pyridylmethyl)ethylendiamine-N'-acetate). A peroxidase-type mechanism, in other words, involvement of iron(IV)oxo species, is consistent with the rates and product distribution. Accordingly, O2, tert-butanol, and cumyl alcohol are concurrently produced for substrates tert-butyl hydroperoxide and cumene hydroperoxide, respectively, in the presence of $[Fe(tpena)]^{2+}$ with O₂ yields of 88% and 44%, respectively.



Rate constants for initial O₂ production ([Fe] 0.005 mol %) were measured to 3.66(6) and 0.29(3) mM s⁻¹, respectively. Participating in the mechanism are spectroscopically detectable (UV-vis, EPR, resonance Raman) transient alkyl- and acylperoxide adducts, $[Fe^{III}OOR(tpenaH)]^{2+}$ $[R = C(CH_3)_3$, $C(CH_3)_2$ Ph, C(O)PhCl; $T_{1/2} = 30$ s (5 °C), 20 s (5 °C), 1 s (-30 °C)] with their common decay product $[Fe^{IV}O(tpenaH)]^{2+}$. Concurrently organic radicals proposed to be ROO[•] were detected by EPR spectroscopy. A lower yield of O_2 at 23% with an initial rate of 0.10(3) mM s⁻¹ for the disproportionation of mchloroperoxybenzoic acid is readily explained by catalyst inhibition by coordination of the product m-chlorobenzoic acid. Oxidative decomposition of the alkyl groups by a unimolecular β -scission pathway, favored for cumene hydroperoxide, competes with ROOH disproportionation. Despite the fact that the catalytic disproportionation is effective, external C-H substrates-when they are present in excess of ROOH-can be targeted and catalytically and selectively oxidized by ROOH using $[Fe(tpena)]^{2+}$ as the catalyst.

KEYWORDS: nonheme iron, alkylperoxide disproportionation, iron(IV)oxo, O_2 evolution, catalysis

INTRODUCTION

The most common motif for the active sites of nonheme iron O₂ activating enzymes is a single endogenous Asp or Glu donor accompanied by 1-3 His and exchangeable water molecules.^{1,2} It can be reasonably expected that the anionic carboxylato coligand will tune physical properties, not least redox potentials, with consequences for the activation of coordinated terminal oxidants. Biology provides examples: the shift from reversible O2 binding in hemerythrin to O2 activation and catalysis of oxidations by the related enzymes methane monooxygenase and ribonucleotide reductase.² The same effects are observed by tuning of the axial endogeneous amino acid donor for heme systems.³ Despite these biological precedents, reports of biomimetic terminal oxidant activation using iron complexes of multidentate ligands containing a carboxylato donor remain relatively few by comparison to the considerable volume of work over the last three decades for iron complexes based on neutral aminopyridyl N-donor-only ligands.⁴⁻⁶ Our efforts to fill this gap have revealed that iron complexes of glycyl-substituted tetra-, penta-, and hexadentate

aminopyridyl ligands activate a range of oxidants including O_{27}^{7} H₂ $O_{27}^{7,8}$ PhIO,^{9,10} and methyl-morpholine-N-oxide,¹ with reactivity patterns that are distinct from those found for counterpart iron complexes based on neutral N4-, N5-, and N6-donor-only ligands. In addition, for these systems, water can be primed to act as the O atom donor for the production of oxidizing iron(IV)oxo complexes by electrochemical¹¹ or Ce(IV)¹² activation in aqueous solutions. Water is ultimately also the terminal source for the O atom of an iron(IV)oxo complex of a monocarboxylato chelating ligand that can oxidize alcoholic substrates in gas phase reactions.¹³ These results point to the carboxylate donor in the first coordination sphere of iron catalysts and enzymes having an important role in tuning oxidant activation.

The iron(III) complex of N, N, N'-tris(2-pyridylmethyl)ethylendiamine-N'-acetate (tpena, Scheme 1) is remarkable

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Scheme 1. Selective Switching between Hydrogen Atom Abstraction (HAT) or Oxygen Atom Transfer (OAT) Pathways in Substrate Oxidation Using the Monocarboxylato Ligand, tpena^a



"When tpena acts as a pentadentate ligand, a dangling pyridyl group functions as a second coordination sphere base. Undemanding steric requirements of tpena mean that an additional endogenous monodentate ligand (e.g., the oxidant PhIO is shown) can coordinate to a high spin (S = 5/2) seven-coordinated iron atom.^{9,12} The iron(III) resting state is S = 5/2 and S = 1/2 for mer-[Fe(tpena)]²⁺ and fac-[Fe(tpena)]²⁺ (not shown), respectively.¹⁰

in its tunable reactivity for substrate oxidation by Fe^{III}(tpena)oxidant adducts or their iron(IV)-oxo derivatives: Highly efficient catalytic reactions can be directed either exclusively toward hydrogen atom abstraction (HAT) or oxygen atom transfer (OAT) mechanisms depending on the choice of terminal oxidant and reaction conditions. Both reaction types are pertinent for rationalizing the impressive scope of reactivity found for the nonheme enzymes, and the Fe-tpena system is unique in its ability to effectively model both of these oxidative pathways. At first sight this is surprising given that tpena is a potentially coordinatively saturating hexadentate ligand. However, structural flexibility on the part of the ligand and geometrical and spin-state flexibility on the part of the iron play crucial roles. The tpena can act as a hexadentate N5O ligand in six- or seven-coordinated iron complexes ([Fe- $(\text{tpena})]^{2+,10}$ [FeOIPh(tpena)]^{2+,9} and [FeOH(tpena)]^{2+,12}) and as a pentadentate N4O ligand in six-coordinated iron complexes ([FeCl(tpenaH)]^{2+,8} and [Fe₂(μ -O)-(tpenaH)₂]^{2+,9}). In this latter group one specific pyridyl arm is uncoordinated and protonated in all crystal structures.^{8-10,12,14} This allows for the creation of another important biomimetic motif-a second coordination sphere base.

Iron(III)-hydroperoxide and iron(III)-peroxide adducts of the iron complexes of the closely related 2-alkylpyridinesubstituted ethylenediamine-backboned neutral N5/N6 donor ligands (Rtpen = N'-alkyl-N,N,N'-tris(2-pyridylmethyl)ethylenediamine, R = Me, Et, Bz, Pr, ⁱPr, Ph, 2-methylpyridine) as well as those for the aforementioned carboxylate-containing $[Fe(tpena)]^{2+}$ have been spectroscopically characterized.^{7,8,15-17} A significant difference in the chemistry of these comparative N5/N6 and N5O systems is evident. For example, $[Fe(tpena)]^{2+}$ catalyzes highly effective alcohol oxidation by H_2O_2 and, in the absence of alcohol or another substrate, H_2O_2 disproportionation.⁸ By contrast the N5/N6 ligand-supported $[Fe(Rtpen)]^{2+}$ systems catalyze neither H_2O_2 disproportionation nor alcohol oxidation by H_2O_2 . In fact, methanol can be used as a solvent for observing transient $[Fe^{III}OOH(Rtpen)]^{2+}$ where half-lives of minutes to hours (rt, room temperature) are found for these complexes. In understanding the effects of the introduction of a carboxylate group into the first coordination sphere of the iron atom for the activation of terminal oxidants located *cis* to this donor, we now turn to the activation of alkyl hydroperoxides and peracids by $[Fe(tpena)]^{2+}$.

Understanding the reactivity of alkyl peroxides is important because they are used as initiators for curing (polymerization) resins and two-component paints.¹⁸ This process involves mixing alkyl peroxide solutions with the vinylester/styrene resin containing any of a wide range of metal catalysts. Alkyl peroxides are used specifically for these applications since they are believed not to undergo disproportionation with the consequent limitations on shelf life, as is the case for the cheaper oxidant H₂O₂.¹⁹ Solutions containing cumene hydroperoxide are sold under the trademark Trigonox K-90 or Trigonox 239a. Alkyl peroxides are also used extensively as terminal oxidants in industrial- and laboratory-scale organic syntheses.²⁰⁻²⁸ Disproportionation of the alkyl peroxides has been sporadically suggested as a possible reason for reduced yields in catalytic selective substrate oxidations;²⁹⁻³² however, the impact of unproductive reactions has never been evaluated in detail nor the release of product O₂ directly measured.

Here, we describe the spectroscopic detection of catalytically competent iron(III)alkylperoxide adducts of [Fe(tpena)]²⁺, their decay product, [Fe^{IV}O(tpenaH)]²⁺, along with concomitantly produced organic radicals that are present in working solutions. ROOH dismutation is unexpected in contrast to H_2O_2 dismutation which is commonly catalyzed by metal salts and complexes.³³⁻³⁷ The quantification of the products of the disproportionation of ROOH, and an analysis of competing selective C-H oxidation reactions involving the R group or an external C-H substrate, allows us to propose a common mechanism for $[Fe(tpena)]^{2+}$ -catalyzed H_2O_2 and ROOH dismutation and external substrate C-H oxidations. Significantly, the reactivity patterns imply a radical character for [Fe^{IV}O(tpenaH)]²⁺, reinforcing our recent observation when this species is produced electrochemically in the absence of terminal chemical oxidants.¹¹ In this case the reactivity of this carboxylate-coordinated iron(IV)oxo toward C-H substrates with increasing C-H bond dissociation energies parallels that of the hydroxo (HO•) radical, albeit with slower rates, no doubt because of size. The results presented here broaden significantly the scope of reactivity observed for nonheme iron models.

EXPERIMENTAL SECTION

Materials and Preparation. N,N,N'-tris(2pyridylmethyl)ethylendiamine-N'-acetic acid (tpenaH), $[Fe_2O(tpenaH)_2](ClO_4)_4(H_2O)_2$, and $[FeCl(Metpen)]PF_6$ (Metpen = N-methyl-N,N',N'-tris(2-pyridylmethyl)ethane-l,2diamine) were prepared as previously described.^{9,38,39} Solutions of *t*-BuOOH (70% in H₂O), *t*-BuOOH in decane (5.5 M), and cumylOOH (88% in cumene) were used as well as *m*-CPBA (77% in *m*-CBAH). Iodometric titrations and NMR spectroscopy were used to confirm the concentration and purity of the peroxide solutions. ¹⁸O-H₂O was supplied by Rotem Industries Ltd., and all other chemicals were purchased from Sigma-Aldrich.

Generation of $[Fe(OOR)(tpenaH)]^{2+}$ (R = C(CH₃)₃, C(CH₃)₂Ph, C(O)PhCl). [Fe₂O(tpenaH)₂](ClO₄)₄(H₂O)₂ was dissolved in acetonitrile, and the solution was allowed to equilibrate for 15 min to maximize the concentration of the solution-state monomeric species $[Fe(tpena)]^{2+}$ that is derived by dehydration of the hemihydrate $[Fe_2O(tpenaH)_2]^{4+}$. Solutions of alkyl or acyl hydroperoxide were subsequently added to generate [Fe(OOR)(tpenaH)]²⁺. Spectroscopic characterization with UV-vis, rRaman, EPR, and Mössbauer spectroscopy were performed on 2-5 mM [Fe] solutions with 50 equiv of alkyl or acyl hydroperoxide. Catalytic experiments were performed on 1 mM [Fe(tpena)]²⁺ (d_3 -MeCN) with 750 equiv of alkyl- or acyl-hydroperoxide and 750 equiv of benzyl alcohol or toluene at rt. Volumetric measurements are performed at rt on either 0.5 mM [Fe] with 1000 equiv of oxidant or 25 μ M [Fe] with 20 000 equiv of oxidant (timedependent detection).

Instrumentation. UV-vis spectra were recorded in 1 cm quartz cuvettes either on an Agilent 8453 spectrophotometer with an UNISOKU CoolSpeK UV USP-203 temperature controller or with an Analytikjena Specord S600 with a Quantum Northwest TC 125 temperature controller. Raman spectra were recorded in 1 cm quartz cuvettes with temperature control using a Flash300 instrument (Quantum Northwest) either at 532 nm (300 mW at source, Cobolt Lasers) or at 785 nm using a PerkinElmer RamanFlex fiber optic coupled Raman spectrometer (90 mW at sample). Data were recorded and processed using Solis (Andor Technology) with spectral calibration performed using the Raman spectrum of MeCN/toluene (50:50 v/v). EPR spectra (X-band) were recorded on a Bruker EMX Plus CW spectrometer (modulation amplitude, 10 G; attenuation, 10 dB) on frozen solutions at 110 K. eview4wr and esimX were used for simulation.⁴⁰ ¹H NMR (400.12 MHz) and ¹³C NMR (100.61 MHz) spectra were recorded on a Bruker Avance III 400 spectrometer at ambient temperature. Chemical shifts are denoted relative to the residual solvent peak (d_3 -MeCN, $\delta_{\rm H}$ = 1.94 ppm and $\delta_{\rm C}$ = 1.32 ppm), and the catalytic experiments were performed directly in MeCN- d_3 on 1 mM [Fe] solutions. Substrate conversion is based on integrals of the aromatic protons. Headspace FTIR spectra were recorded in sealed 1 cm quartz cuvettes on a JASCO FT-NIR/MIR-4600 spectrometer, and the CO₂ signal was quantified as previously described.⁸ Mössbauer spectra were recorded at 80K on a conventional spectrometer with alternating constant acceleration of the γ -source. Isomer shifts are denoted relative to α iron at 298 K, and the sample temperature was maintained constant in an Oxford Instruments Variox cryostat. The ysource (57Co/Rh, 1.8 GBq) was kept at room temperature. The mf.SL package⁴⁰ was used to fold the spectra hereby merging the two linear halves of the raw data and to eliminate the parabolic background as well as fitting the data. ESI-MS spectra were recorded in high-resolution positive mode with a Bruker microTOF-QII mass spectrometer. MIMS spectra were recorded using a Prisma quadrupole mass spectrometer (Pfeiffer Vacuum, Asslar, Germany). A flat sheet membrane $(250 \,\mu\text{m})$ of polydimethylsiloxane (Sil-Tec sheeting, Technical Products, Decatur, GA) separated the vacuum chamber $(1 \times$ 10^{-6} mbar) from the solution in the sample chamber (total volume 2.5 mL), which was equipped with magnetic stirring. The reaction chamber was filled with solutions of [Fe-

(tpena)²⁺, and the alkyl peroxide was injected directly to the solutions in the sample chamber as the resulting gas evolution was simultaneously measured. The data were recorded and processed using Quadstar 422 (Pfeiffer Vacuum, Asslar, Germany). Volumetric measurements were performed using a two-neck round-bottom flask with a stopcock-equipped gas delivery tube connected to a gas-measuring buret (± 0.1) mL). The peroxides were injected through a septum, and the evolved O₂ was volumetrically measured as a function of time. The rate constants reported represent the mean value of minimal double determinations which fall within $\pm 5\%$. Analyte solutions of peroxide (500 µL), 1.64 M KI(aq) (5 mL), 20% $H_2SO_4(aq)$ (5 mL), and H_2O (25 mL) were prepared for iodometric titrations (±0.1 mL). An ammonium molybdate solution [0.5 mL, prepared from (NH₄)₆Mo₇O₂₄ (9 g), NH₃(aq) (28-30%, 5 mL), NH₄NO₃ (24 g), and H₂O (5 mL)] and a starch solution (1 g/100 mL) were added as catalyst and indicator, respectively. The mixture was titrated with 0.3 M $Na_2S_2O_3(aq)$, and the analysis was repeated three times.

RESULTS AND DISCUSSION

Iron(III)-alkyl Peroxides, [Fe(OOR)(tpenaH)]²⁺ R = C(CH₃)₃ and CH(CH₃)₂Ph. The solid-state precursor for the solution-state chemistry described below is the dark brown $[(tpenaH)Fe(\mu-O)Fe(tpenaH)](ClO_4)_4$.⁹ On dissolution this oxo-bridged complex equilibrates with monomeric species: a hydrate, [Fe^{III}(OH)(tpenaH)]^{2+,12} and a dehydrate, $[Fe^{III}(tpena)]^{2+,10}$ Cleavage of the oxo-bridge is accompanied by a color change from yellow-brown (λ_{max} 258 nm) to red-orange (λ_{max} 360 nm) in acetonitrile and takes ca. 15 min to equilibrate at rt.¹⁰ The addition (50 equiv) of *tert*-butyl hydroperoxide (t-BuOOH, 70% aq solution) or cumene hydroperoxide (cumylOOH, 88% solution) to these equilibrated solutions triggers an immediate color change to purple $(\lambda_{\text{max}} 558 \text{ nm})$ or red $(\lambda_{\text{max}} 531 \text{ nm})$, respectively (Figure 1a, Table 1). Gas evolution is concomitant. This is predominantly O₂, vide infra. The chromophores are ascribed to the transient species [Fe(OO-t-Bu)(tpenaH)]²⁺ and [Fe(OOcumyl)-(tpenaH)]²⁺, respectively. With reference to the crystal structures of $[Fe(Cl)(tpenaH)]^{2+,8}$ [(tpenaH)Fe(μ -O)Fe-(tpenaH)]^{4+,9} [V(O)(tpenaH)]^{2+,12} and [Cr(O₂)- $(tpenaH)]^{2+,14}$ the incoming ROOH is proposed to form a "charge-separated" adduct with $[Fe(tpena)]^{2+}$; i.e., the alkylperoxide is deprotonated and bound to iron(III), and the proton protonates an uncoordinated pyridine group. While it seems that an initial dehydration of the starting hemihydrate is necessary to observe these transients, counterintuitively, the formation of the iron-alkylperoxide adducts is dependent on the presence of a small amount of water. [Fe(OO-t-Bu)(tpenaH)]²⁺ is not detected if the *t*-BuOOH is supplied in decane (5.5 M). If, however, 4 equiv of water is introduced to the equilibrated acetonitrile solutions containing monomeric [Fe(tpena)]²⁺/[Fe(OH)(tpenaH)]²⁺ immediately prior to the addition of the decane solution of t-BuOOH, the formation of the iron alkyl peroxide species is reinstated. These observations suggest that it is the mononuclear hydrate, $[Fe(OH)(tpenaH)]^{2+}$, rather than $[Fe(tpena)]^{2+}$ that is the immediate precursor for reaction with ROOH, and that the reaction involves substitution of a hydroxo ligand by the incoming alkylperoxide (Scheme 2) rather than an alkylperoxido displacement of a chelating pyridine group as would be the case if [Fe(tpena)]²⁺ was the immediate precursor. We



Figure 1. Spectroscopic data of the [Fe(OOR)(tpenaH)]²⁺ generated by addition of 50 equiv of *t*-BuOOH or cumylOOH to $[Fe(tpena)]^{2}$ in MeCN. (a) UV-vis absorption spectra (5 °C) of [Fe(OO-t- $Bu)(tpenaH)]^{2+}$ (blue, [Fe] = 2 mM) and [Fe(OOcumyl)-(tpenaH)²⁺ (red, [Fe] = 4 mM). Inset: photograph of frozen samples of [Fe(OO-t-Bu)(tpenaH)]²⁺ and [Fe(OOcumyl)-(tpenaH)]²⁺. (b) EPR spectrum (black) recorded on a frozen solution of [Fe(OO-t-Bu)(tpena)]²⁺ in MeCN at 110 K. Microwave frequency 9.314 212 GHz. Fitted data for [Fe(OO-t-Bu)(tpenaH)]²⁺ and the t-BuOO[•] radical are shown in blue and green, respectively. (c) Resonance Raman spectra of [Fe(OO-t-Bu)(tpenaH)]²⁺ (blue, $\lambda_{\text{exc}} = 785, -25 \text{ °C}, 3 \text{ mM}$ and its decay product (purple, $\lambda_{\text{exc}} = 785$), and $[Fe(OOcumyl)(tpenaH)]^{2+}$ (red, $\lambda_{exc} = 532, -25$ °C, 2 mM) and its decay product (orange, $\lambda_{exc} = 532$). * = solvent band from MeCN, # = bands from either t-BuOOH or cumylOOH. The spectra are normalized to the solvent band at 919 cm⁻¹.

Table 1. Spectroscopic Properties for $[Fe^{III}OOR(tpenaH)]^{2+}$

R	λ_{\max} [nm]	$[cm^{-1}]$	$[cm^{-1}]$	g-values
$C(CH_3)_3$	558	675	786	2.20, 2.12, 1.97
$CH(CH_3)_2Ph$	531	684	782	2.19, 2.12, 1.97
C(O)m-ClPh	565	а	а	2.23, 2.18, 1.95
^a Lifetime too sł	nort for me	easurement at	−40 °C.	

have previously shown that two diastereoisomers (a *mer* and *fac* in terms of the three pyridine donors) for $[Fe(tpena)]^{2+}$ coexist in solution.^{8,10} Hydration will convert them to the same conformer, and the simplicity of the spectroscopy, *vide infra*, supports the formation of only one diastereoisomer for the alkylperoxide adducts. Our representation of $[Fe(X)-(tpenaH)]^{2+}$, X = OH, OO-*t*-Bu, OOcumyl (Scheme 2), depicts therefore the diastereoisomer containing the pentadentate tpena conformation analogous to that found in all the known crystal structures of $\{MX(tpenaH)\}^{n+.8-10,12,14}$ In these, the glycyl donor is located *cis* to the exogenous ligand which in turn is *trans* to the amine donor associated with the dipyridylamine moiety.^{8,9,12}

The iron(III)-alkylperoxide species are short-lived at room temperature (seconds); however, a $T_{1/2}$ of 30 and 20 s for [Fe(OO-t-Bu)(tpenaH)]²⁺ and [Fe(OOcumyl)(tpenaH)]²⁺, respectively, is measured at 5 °C (Figure S1). At -30 °C both species can be detected for several minutes using the same ratios and concentrations of reagents. Solutions containing ca. 10% water gave the maximum yield in terms of the lifetime of the alkyl peroxides, which increased from 3 to 6 min at -15 °C. EPR spectra of frozen solutions show rhombic signals with g = 2.20, 2.12, and 1.97 and g = 2.19, 2.12, and 1.97 for [Fe(OO-t-Bu)(tpenaH)]²⁺ (Figure 1b) and [Fe(OOcumyl)(tpenaH)]²⁺ (Figure S2), respectively, indicating low-spin iron(III) (S = 1/2) species. Resonance Raman spectra show enhanced bands at 675 and 786 cm⁻¹ for $[Fe(OO-t-Bu)(tpenaH)]^{2+}$ and at 684 and 782 cm⁻¹ for $[Fe(OOcumyl)(tpenaH)]^{2+}$ (Figure 1c). On the basis of a comparison with the spectra of previously reported low-spin mononuclear nonheme iron(III) alkyl peroxide species, these bands can be associated with the Fe-O and O-O bonds. respectively.^{41,42} The visible absorbance bands are red-shifted compared to the hydroperoxide-derived species [Fe(OOH)-(tpenaH)]²⁺ (λ_{max} 520 nm). The O–O stretch of the [Fe(OOR)(tpenaH)]²⁺ complexes was not shifted compared to that observed for $[Fe(OOH)(tpenaH)]^{2+}$ (788 cm⁻¹),⁸ whereas the Fe-O stretches are found at 70 cm⁻¹ higher wavenumbers suggesting a comparatively stronger Fe-O bond. A similar trend was noted for the Raman shift of the homologous $[Fe(OOR)(TPA)(solvent)]^{2+}$ (R = H, t-Bu) pair.^{41,43} A band at 484 cm⁻¹ for [Fe(OO-t-Bu)(tpenaH)]²⁺ can be assigned to a combined O-C-C/C-C-C bending vibration from the *t*-Bu group.⁴³

Evidence for Homolytic FeO–OR Bond Cleavage in Alkylperoxide Adducts. The decay of the $[Fe(OOR)-(tpenaH)]^{2+}$ complexes proceeds by homolytic cleavage of the Fe^{III}O–OR bond. This conclusion is supported by the evolution of the characteristic 730 nm band^{11,12} for $[Fe^{IV}O-(tpenaH)]^{2+}$ (Figure 2a). Combined time-resolved UV–vis and rRaman spectroscopy of the decaying $[Fe^{III}OOR-(tpenaH)]^{2+}$ species shows that a resonance-enhanced band at 863 cm⁻¹ (Figure 1c) can be correlated to the 730 nm band





Figure 2. Conversion of $[Fe(OO-t-Bu)(tpenaH)]^{2+}$ to $[Fe^{IV}O(tpenaH)]^{2+}$ (50 equiv of *t*-BuOOH, [Fe] = 2 mM, 5 °C). (a) Time-dependent UV-vis absorption spectra. Inset: time-trace for absorbance at 558 nm (blue) and 730 nm (green). (b) Time dependence of absorbance at 558 and 730 nm as portions of 50 equiv of *t*-BuOOH are added every 100 s to regenerate $[Fe(OO-t-Bu)(tpenaH)]^{2+}$ and $[Fe^{IV}O(tpenaH)]^{2+}$.

in the UV–vis spectrum, and it is therefore assigned to a $\nu_{\rm Fe=O}$ stretch. This value is higher than Raman shifts previously reported for nonheme iron(IV)oxo species which typically occur in the range 790-850 cm⁻¹ for both S = 1 and S = 2systems,⁴⁴ suggesting an Fe=O bond that is stronger than typically found for nonheme iron(IV)oxo systems. We speculate that the bond possesses partial triple bond character analogous to that proposed for vanadyl complexes.⁴⁵⁻⁴⁷ Significantly, isotropic signals at g = 2.02 (Figure 1b) and g = 2.00 (Figure S2) for $[Fe(OO-t-Bu)(tpenaH)]^{2+}$ and $[Fe(OOcumyl)(tpenaH)]^{2+}$, respectively, overlap with the signals from the low-spin Fe(III)-hydroperoxide adducts in the EPR spectra. These are due to production of an organic radical. Homolysis of the Fe^{III}O-OR bond produces the immediate sister products [Fe^{IV}O(tpenaH)]²⁺ and the alkoxide radicals $^{\circ}$ O-*t*-Bu or $^{\circ}$ OC(CH₃)₂Ph, respectively. These latter species can be expected to be too short-lived for detection, and in the presence of excess ROOH they can be expect to abstract a peroxy H atom to give •OO-t-Bu and •OOC(CH₃)₂Ph, respectively, along with the derived alcohol.^{48,49} The isotropic EPR signals are therefore assigned to these generated peroxy radicals rather than the directly produced alkoxide radicals. Signals due to the Fe(IV)oxo species and the organic radicals are present concurrently with those for $[Fe(OOR)(tpenaH)]^{2+}$ (Figures 1b and 2) indicating similar stabilities for the two iron-based transients. Supporting the coexistence of iron(III)

hydrates, an iron(III)alkylperoxide, and an iron(IV)oxo species is a Mössbauer spectrum (Figure S3) of [Fe(OH)(tpenaH)]²⁺ and 50 equiv of cumylOOH, frozen 20 s after mixing. This can be fitted to $[Fe(OH)(tpenaH)]^{2+}$ ($\delta = 0.14 \text{ mm s}^{-1}$, $\Delta E_Q = 2.08 \text{ mm s}^{-1}$, 22%), $[Fe_2O(tpenaH)_2]^{4+}$ ($\delta = 0.43 \text{ mm s}^{-1}$, $\Delta E_Q = 1.60 \text{ mm s}^{-1}$, 26%), and $[Fe^{IV}O(tpenaH)]^{2+}$ ($\delta = 0.00$ mm s⁻¹, $\Delta E_Q = 0.90$ mm s⁻¹, 24%) which have been independently characterized previously by Mössbauer spectroscopy.¹² This has allowed for assignment of a fourth species to the low-spin iron(III)alkylperoxo complex [Fe(OOcumyl)-(tpenaH)]²⁺ (δ = 0.20 mm s⁻¹, ΔE_Q = 2.00 mm s⁻¹, 28%). These parameters are quite similar to those for [Fe(OOH)-(tpenaH)]²⁺ ($\delta = 0.21 \text{ mm s}^{-1}$, $\Delta E_Q = 2.08 \text{ mm s}^{-1}$).⁸ After their decay, all species, $[Fe(OOR)(tpenaH)]^{2+}$, $[Fe^{IV}O-$ (tpenaH)]²⁺, and the organic radicals, are regenerated by addition of further portions (50 equiv) of alkyl hydroperoxides (Figure 2b). The repeatable cyclability is evidence that tpena is not oxidatively degraded, and this stands in contrast to the dismutation reaction of H_2O_2 catalyzed by $[Fe(tpena)]^{2+}$ where tpena will start decomposing when the substrate H_2O_2 is not present in a large excess, or alternatively, if an easily oxidizable sacrificial substrate is not provided.⁸ In the present case the organic groups of the alkyl hydroperoxides offer builtin sacrificial exogenous substrates to compete with the alkyl hydroperoxide dismutation and herewith effectively competitively inhibit tpena degradation. The solid-state precursor



Figure 3. Detection of evolved O_2 and CO_2 , when ROOH is added to $[Fe(OH)(tpenaH)]^{2+}$ in MeCN. (a) MIMS spectra of $[Fe(OH)(tpenaH)]^{2+}$ (black) and with the addition of 50 equiv of cumylOOH after 2 min (red) and 12 min (blue). The broad peak between m/z = 35 and 42 is due to actionitrile. The m/z = 43 signal originates from unreacted cumylOOH passing through the membrane. Inset: time dependence of the ion current for the ions $O_2^{\bullet+}$ (m/z 32). [Fe] = 0.5 mM. (b) Time-trace of the O_2 evolution (1556 cm⁻¹) with headspace Raman spectroscopy ($\lambda_{exc} = 532$ nm) with the addition of two portions of 100 equiv of *t*-BuOOH. [Fe] = 2 mM. The arrows indicate addition of *t*-BuOOH. Build-up of pressure in the sealed cuvette prevented further additions of the peroxide to the closed system; however, the gas evolution can be reinitiated more than 10 times using an open vessel. (c) Time-dependent volumetric detection of the gas release with the addition of 20 000 equiv of oxidant to 25 μ M [Fe(OH)(tpenaH)]²⁺ solutions in MeCN: *t*-BuOOH (blue), cumylOOH (red), and *m*-CPBA (green). (d) Time-resolved headspace FTIR spectroscopy showing the evolution of CO₂ over time after addition of 1000 equiv of cumylOOH. Time-dependence of absorbance at 2360 cm⁻¹. Red, 1000 equiv of cumylOOH; blue, 1000 equiv of *t*-BuOOH. [Fe] = 0.5 mM. The bands at 2253 and 2292 cm⁻¹ are due to acetonitrile.

[(tpenaH)Fe(μ -O)Fe(tpenaH)](ClO₄)₄ can be quantitatively recovered after the consumption of thousands of equivalents of alkyl peroxides.

Catalytic Alkyl Hydroperoxide Disproportionation and Competing Radical Reactions. Simultaneous with detection of [Fe^{III}(OOR)(tpenaH)]²⁺ and [Fe^{IV}O(tpenaH)]²⁺, colorless gas production is visible as bubbles when the alkyl peroxides are added in excess to $[Fe(OH)(tpenaH)]^{2+}$ in acetonitrile (e.g., 50 equiv of ROOH to 0.5 mM [Fe]) (see Video S1). Membrane-introduction mass spectrometry (MIMS) (m/z 32, Figure 3a) and headspace Raman spectroscopy (O=O band at 1556 cm⁻¹, Figure 3b) confirmed that this is predominantly O2. That this was the result of water oxidation of adventitious water, and that provided in the aqueous solutions of peroxides, was excluded because of inappropriately large amounts of O2 released compared to the water available, and the lack of ¹⁸O incorporation in the evolved O_{21}^{50} when ¹⁸O-labeled water was added to mixtures. In addition, this experiment demonstrates that the rate of ROOH disproportionation is faster than any potential O atom exchange between water and the $[Fe^{IV}O(tpenaH)]^{2+}$: The evolved O₂ derives exclusively from the disproportionation of the alkyl hydroperoxides, and the reaction is catalytic. O_{2} , in lower yields, evolves also when

water is the sole solvent; however, in this case the iron-based transients cannot be observed. The oxo-bridged complex dominates the speciation in these solutions, and this observation supports the conclusion that this cannot directly activate ROOH and corroborates the deduction that the catalytically competent resting-state complex is [Fe(OH)-(tpenaH)²⁺. The addition of 1000 equiv of t-BuOOH (aq 70%) to a $[Fe(tpena)]^{2+}$ solution (3 mL 0.5 mM) results in the production of 15.5(2) mL of gas (Table 2). The addition of a second portion of 1000 equiv results in a release of another 15.5(2) mL. This includes a very small amount of CO_2 , vide infra, and when this is accounted for, the yield of O_2 is approximately 88% (assuming that 2 mol of t-BuOOH are required to yield 1 mol of O_2). The equivalent experiment using cumylOOH gives a lower yield of O_2 at 44% (8.0 mL). Concurrent tert-butanol and cumyl alcohol production as the major organic products, respectively, was confirmed using NMR spectroscopy to follow *in situ* reactions in d_3 -MeCN. Spectra recorded 1 h after the addition of alkyl hydroperoxide showed that the t-BuOOH and cumylOOH were fully consumed, and gas evolution had ceased (Figures S4 and S5).

Sugimoto and Sawyer⁵¹ have shown that simple iron perchlorates catalyze H_2O_2 dismutation in acetonitrile under anhydrous conditions. In a significant contrast they do not

Table 2. Volumetric Measurements of O_2 and CO_2 Were Performed on 0.5 mM [Fe(OH)(tpenaH)]²⁺ with the Addition of Either *t*-BuOOH, CumylOOH, or *m*-CPBA (1000 equiv)^{*a*}

	V _{gas} [mL]	yield of O ₂ adjusted for CO ₂ release	ratio of ROOH and products, ^b ROOH:ROH:ketone
t-BuOOH	15.5 ± 0.2	15.1	0:0.95:0.05
cumylOOH	8.0 ± 0.4	7.6	0:0.70:0.30
m-CPBA	4.0 ± 0.4	3.7	0.50:0.50:0

^{*a*}The ratio of organic products was determined by *in situ* NMR experiments using $[Fe(OH)(tpenaH)]^{2+}$ (1 mM in MeCN- d_3) and the addition of 750 equiv of oxidant. ^{*b*}After 1 h of reaction time in the absence of external substrates.

promote *t*-BuOOH or *meta*-chloroperoxybenzoic acid (*m*-CPBA) disproportionation.⁵² Our checks as a control for the present context verify this earlier work, also when water is present. In lieu of a known catalyst for *t*-BuOOH disproportionation with which to compare the efficiency of $[Fe(tpena)]^{2+}$, we tested $[FeCl(Metpen)]PF_6$ for its ability to catalyze this reaction. This complex is a highly pertinent system for comparison since with its ethylene backbone it is structurally related, and importantly, iron(III) hydroperoxide

adducts have been characterized for this and related Rtpen (R = Me, Bz, Et, Pr, *i*-Pr, Ph) species.^{15–17,53–55} Using the same ratios of $[FeCl(Metpen)]^+$:*t*-BuOOH and conditions as those above for the Fe-tpena system ([Fe] = 0.5 mM, 1000 equiv of tBuOOH) we found no detectable disproportionation of *t*-BuOOH; i.e., over 30 min, no O₂ had evolved.

Volumetric monitoring of the release of the O_2 as a function of time revealed that the initial rate constants are 3.66(6) and 0.29(8) mM s⁻¹ (3 mL of 25 μ M [Fe] and 20 000 oxidant/ substrate) for the addition of t-BuOOH and cumylOOH, respectively; hence, the initial rate is 12 times faster for t-BuOOH (Figure 3c). The O₂ release ceases after 5 min when employing t-BuOOH, whereas this takes several hours when cumylOOH is used under the same concentrations. At constant complex concentration saturation kinetics were not observed on the addition of 6500-30 000 equiv of t-BuOOH, and the relationship between catalyst concentration and the rate constants is nonlinear: A doubling of the iron concentration results in a more than doubling of the rate constants (Figures S6-S8). The initial lag time before the O_2 releases is rationalized by the need to establish a steady-state concentration of $[Fe^{IV}O(tpenaH)]^{2+}$ and the alkoxy radical. As mentioned, both t-BuO[•] and cumylO[•] will abstract an H atom from the excess t-BuOOH and cumylOOH, respectively, to

Scheme 3. Catalytic Alkyl Hydroperoxide Disproportionation Using the [Fe(tpena)]²⁺ System^a



^{*a*}Entry in the cycle occurs by the charge separation addition of an alkyl hydroperoxide to form $[Fe^{III}OOCR_3(tpenaH)]^{2+}$, see Scheme 2. (a) Production of $[Fe^{IV}O(tpenaH)]^{2+}$ and alkoxide radical by FeO–OCR₃ homolysis. (b) Reaction of alkylperoxide radical with $[Fe^{IV}O(tpenaH)]^{2+}$ to form the putative $[FeOOOCR_3(tpenaH)]^{2+}$ (c) β -Scission of alkoxy radical. (d) Production of alkylperoxide radical and product alcohol or carboxylic acid. (e) Reaction of alkyl hydroperoxide with $[Fe^{IV}O(tpenaH)]^{2+}$ to give alkylperoxide radical. (f) Ligand exchange of the alcohol adduct to give the alkyl hydroperoxide adduct of $[Fe^{III}(tpena)]^{2+}$. (g) O₂ expulsion and formation of the alkoxy adduct of the resting-state catalyst, $[Fe^{III}OR(tpenaH)]^{2+}$. form the EPR detectable secondary radicals t-BuOO[•] and cumylOO[•]. Acetone and acetophenone, respectively, are detected by NMR spectroscopy as the expected minor organic products from the disproportionation reactions (Table 2, Figures S4 and S5). The formation of these ketone products occurs by β -scission reactions of the alkoxyl radical. In the case of *t*-BuOOH, the acetone formation amounts to ca. 5% of the organic products, whereas for cumylOOH the yield of acetophenone is greater at approximately 30%. This is readily rationalized by the lower stability of cumylO[•] compared with *t*-BuO^{•.56} Hence the β -scission pathway, being unimolecular, is more pronounced when cumvlOOH is a substrate, and cumylOOH disproportionation is less favored than the disproportionation of t-BuOOH. The addition of further portions of alkyl hydroperoxides reinitiates O₂ evolution (Figure 3b) concomitant with the visible regeneration of the iron(III)-peroxide species (Figure 2b). The catalyst is robust.

As mentioned in the Introduction, the cause of low yields in redox-active metal (Rh, Fe)-complexes catalyzing oxidations of organic substrates by alkyl hydroperoxides have sporadically been ascribed—without experimental verification—to a putative background dismutation.^{29–31} Aside from the oxidation of organic substrates, alkyl hydroperoxides are routinely used in the preparation of high-valent metal complexes. In these syntheses it would seem that ample opportunities for the observation of disproportionation have been available to the many workers in the area of high-valent biomimetic first-row transition metal complexes: The dearth of observations of this specific reaction is surprising. Over two decades ago Caudle et al. showed that Mn^{III}₂(2-OHsalpn)₂ (2- $OHsalpn = 1,3-bis(salicylideneamino)-2-propanol)^{57}$ reacts with t-BuOOH to give a $Mn^{III}(O)Mn^{IV}$ complex. These authors assumed that the concurrently produced t-butoxy radical (undetected) reacts with excess t-BuOOH to give the tbutylperoxyl radical (eq 1). Subsequent coupling of two tbutylperoxyl radicals was proposed as the source of the observed O_2 (eq 2). O_2 evolution from alkyl hydroperoxides was noted also when they are reacted with $[Fe(tpa)X_2]^{2+}$ and $[Fe_2O(tpa)_2(H_2O)_2]_4$ (X = Cl, Br; tpa = tris(2-pyridylmethyl)amine)⁵⁸). In these cases, peroxy H atom abstraction from ROOH to produce ROO[•] by the iron(III)-tpa complex with concurrent reduction of the iron to the +2 state was proposed to initialize the reaction. Again, O2 extrusion after the ROO[•] coupling reaction in eq 2 was proposed. In contrast to the tpena-based system here, high-valent iron is not involved. O₂ was not quantified in either of these studies so we cannot compare yields or rates. Neither of these reactions were studied in detail from the viewpoint of actual turnover or catalysis.

 $^{\bullet}\text{O}-t-\text{Bu} + t-\text{BuOOH} \rightarrow t-\text{BuOH} + ^{\bullet}\text{OO}-t-\text{Bu}$ (1)

$$2^{\circ}$$
OO-t-Bu \rightarrow t-BuOOOO-t-Bu \rightarrow O₂ + 2° O-t-Bu (2)

While the coupling of •OOR radicals (eq 2) might be one pathway to O_2 , the reaction mixtures contain an abundance of competing substrates to potentially quench •OOR, not least the oxy-radical-like [Fe^{IV}O(tpenaH)]^{2+,11} We propose that the major O_2 releasing step could predominantly involve the coupling of [Fe^{IV}O(tpenaH)]^{2+,11} with the abundantly present •OOCR₃. Extrusion of O_2 , from a putative [Fe^{III}OOOCR₃(tpenaH)]²⁺ reminiscent of the Russell mechanism's dialkyltetroxide intermediate in eq 2,⁵⁹ will collapse to O_2 and an iron(III)-alkoxide, [Fe^{III}OCR₃(tpenaH)]²⁺ (Scheme 3 path g). The beauty of this proposal is that all the detected products are accountable by the pathways in Scheme 3.

Concurrently with the alkyl hydroperoxide decomposition and generation of O₂ (m/z = 32), an increase of the peaks at m/z 29, 30, 31, and 44 in MIMS spectra is observed suggesting formation of one-carbon-containing molecules (Figure 3a). Decomposition of tpena as the carbon source is excluded, because of (i) the repeatability over many cycles without loss of catalytic efficiency, (ii) the fact that $[(tpenaH)Fe(\mu$ -O)Fe(tpenaH)](ClO₄)₄ can be quantitatively recovered, and (iii) the ratio of the alkyl derived products of the reactions. Acetonitrile oxidation as the source is also discounted because of the relatively high BDEs for H-CH₂CN and H₃C-CN $(406 \text{ and } 522 \text{ kJmol}^{-1})^{60}$ as well as the obvious lack of correlation to concentration. The remaining and most plausible option is that the methyl radical produced via the β -scission pathway is the source (Scheme 3, path c). This methyl radical can react with O2 (which saturates the solutions) to give carbon monoxide, carbon dioxide, formaldehyde, and methanol.^{61,62} The exact ratio between these products will be pressure- and temperature-dependent; however, the growth of ions at m/z 29, 30, 31, and 44 in the MIMS spectra for both alkyl hydroperoxides is consistent with formation of formaldehyde, methanol, and CO_2 (Figure S9). Crucially, the quantity of CO_2 is directly proportional to the amount of ROOH that was added initially. The yield was quantified by headspace FTIR spectroscopy to be approximately 1 CO₂ per 30 ROOH consumed (Figure 3d). This CO_2 accounts for a minor proportion of the gas evolved during the decomposition, and as mentioned above, the determination of O_2 yields has taken this into account.

Competitive and Selective C-H Substrate Oxidation Reactions. If toluene (750 equiv) is added before addition of t-BuOOH (750 equiv) to [Fe(OH)(tpenaH)]²⁺, NMR spectroscopy verifies that it is oxidized to benzaldehyde (Figure S10: $\delta_{\rm H}$ (CHO) = 10.00 ppm and $\delta_{\rm C}$ (CHO) = 193.7 ppm). After 1 h only trace amounts of *t*-BuOOH remain, with t-BuOH being the major product with traces of acetone. On the basis of the comparison of the integrals of the five aromatic protons in toluene and benzaldehyde, a 10% conversion has occurred (TON = 38). Benzylalcohol, which is an intermediate on the reaction pathway from toluene to benzaldehyde, is not detected, presumably because of its facile onward oxidation. Benzoic acid is not detected suggesting that benzaldehyde is not easily oxidized under these conditions. Control reactions show that *t*-BuOOH cannot oxidize toluene, benzyl alcohol, or benzaldehyde in the absence of $[Fe(tpena)]^{2+}$.

The [Fe(OH)(tpenaH)]²⁺/ROOH system furnishes highly selective catalysis of the oxidation of appropriate C-H bonds under appropriate limiting reagent conditions. A conversion of 47% to benzaldehyde after 1 h is measured when benzyl alcohol is added to acetonitrile solutions in equivalent amounts to the subsequently added *t*-BuOOH (PhCH₂OH:*t*-BuOOH: $[Fe(OH)(tpenaH)]^{2+} = 750:750:1$, TON = 352). Volumetric detection of the gas release under these conditions shows a decrease to 8.0 mL compared with the 15.5 mL that could be recovered if an external substrate is not added. Quantification of the CO_2 shows that the same amount of CO_2 is produced as that in the absence of benzyl alcohol; thus, the β -scission pathway is not suppressed in any significant way, and an adjusted yield of 44% O₂ in the presence of equimolar amounts of t-BuOOH and benzyl alcohol can be determined. This correlates nearly perfectly with the 47% conversion of the

benzyl alcohol to benzaldehyde detected by NMR spectroscopy. Hence, PhCH₂OH (BDE for methylene C-H, 331 kJ mol⁻¹⁶⁰) and t-BuOOH (BDE t-BuOO-H, 352 kJ mol⁻¹⁶⁰) compete equally as substrates for [Fe^{IV}O(tpenaH)]²⁺ despite the lower BDE for PhCH₂OH. This implies a polar effect on the HAT process promoting *t*-BuOOH as an equal substrate. It is easy to envisage that the dangling pyridinium arm might participate through a supramolecular H bonding interaction with the distal O atom of the t-BuOOH. A 1:5 ratio of t-BuOOH:PhCH₂OH reduced the gas release further to a 25% of the yield found in the absence of benzyl alcohol. The in situ oxidants responsible for the oxidation of toluene and benzyl alcohol are proposed to be all of $[Fe^{IV}O(tpenaH)]^{2+}$, RO[•], and ROO[•]. These will all abstract H atoms from the aliphatic C-H bonds of these substrates to regenerate [Fe^{III}OH(tpenaH)]²⁺ and ROOH, and produce ROH, along with benzyl radicals with which the generated O₂ might react directly.

O₂ Evolution Is Suppressed in the Reaction of Fe(III)tpena with a Peracid. The reaction of [Fe^{III}(OH)-(tpenaH)]²⁺ with *m*-CPBA (50 equiv) generates [Fe^{IV}O-(tpenaH)]²⁺ more rapidly compared to H₂O₂ and alkyl hydroperoxides as made evident by the appearance of an absorption band at 730 nm, detected only at low temperatures $(-30^{\circ}C)$ where $[Fe^{IV}O(tpenaH)]^{2+}$ shows a half-life of around 20 s. At -40 °C a barely perceptible shoulder at 565 nm is revealed (<2 s, Figure 4a). This is likely due to $[Fe(OOC(O)m-PhCl)(tpenaH)]^{2+}$. The electron-withdrawing properties of the chloro-substituted aromatic acylated system produces a more labile O-O bond than that observed for t-BuOOH and cumylOOH. The same tendency in O-O bond stability has been observed for iron(III) porphyrin complexes of m-CPBA and t-BuOOH.⁶³ The EPR spectra (Figure 4b) recorded on flash-frozen samples of mixtures of [Fe^{III}(OH)-(tpenaH)²⁺ and 50 equiv of *m*-CPBA show three distinct signals: a high-spin iron(III) ($g^{\text{eff}} = 8.2, 5.2, 4.2$); a rhombic low-spin iron(III) with g = 2.23, 2.18, and 1.95 (red); and an isotropic signal with g = 2.00 (blue). The latter two signals can, analogously with the alkyl peroxide reactions, be associated with the transient peroxyacid adduct [Fe(OOC(O)m-PhCl)-(tpenaH)]²⁺ and its daughter *m*-ClPhC(O)O[•] or derived *m*- $ClPhC(O)OO^{\bullet}$ radical. The high-spin signal observed in the EPR spectrum has no counterpart in the reactions with t-BuOOH or cumylOOH, and we propose that this is due to $[Fe^{III}(OC(O)PhCl)(tpenaH)]^{2+}$, vide infra.

While some O_2 is detected, the reaction of [Fe(OH)-(tpenaH)]²⁺ with 1000 equiv of *m*-CPBA does not give rise to the release of large amounts of O_2 as it does in the reactions with t-BuOOH and cumylOOH (Table 2). A yield of 23% of the theoretical O₂ production (based on the mechanism in Scheme 3) is volumetrically detected after 30 min. The products of the disproportionation of m-CPBA are O₂ and mchlorobenzoic acid (m-CBAH). Thus, X in Scheme 3 will be m-chlorobenzoyl. Corroborating, NMR spectra of mixtures containing Fe-tpena and m-CPBA (1:750) in d_3 -MeCN show that *m*-CBAH is produced concurrently with consumption of the m-CPBA. After 1 h of reaction time, half of the m-CPBA has disappeared (Figure S11), but 25% of the m-CPBA remains unreacted after 3 days. It is not unexpected that the product *m*-CBAH might inhibit the catalytic reaction to a far greater degree compared with the product alcohols from the alkylhydroperoxide disproportionation reactions, i.e.; the species $[Fe(OX)(tpenaH)]^{2+}$ in Scheme 3, in this case $[Fe^{III}(OC(O)PhCl)(tpenaH)]^{2+}$, is more stable than the



Figure 4. (a) UV-vis spectra of $[Fe(tpena)]^{2+}$ (orange) with the addition of *m*-CPBA (50 equiv, [Fe] = 2 mM) at -40 °C to generate $[Fe(OOC(O)m\text{-PhCl})(tpenaH)]^{2+}$ (red) and $[Fe^{IV}=O(tpenaH)]^{2+}$ (green). (b) EPR spectra recorded on a frozen solution of $[Fe(OH)(tpenaH)]^{2+}$ with the addition of 50 equiv of *m*-CPBA in MeCN at 110 K. Microwave frequency: 9.309 872 GHz. Fitted data for $[Fe(OOC(O)m\text{-PhCl})(tpenaH)]^{2+}$ and the *m*-ClPhC(O)O[•] or derived *m*-ClPhC(O)OO[•] radical are shown in red and blue, respectively. (c) ESI-MS of a solution of $[Fe(tpena)]^{2+}$ and *m*-CBA (1:50, MeCN). Assignments as follows. *m/z*: calcd for $C_{29}H_{28}ClFeN_5O_4$, $[Fe^{III}(tpena)(m\text{-CBA})]^+$, 601.117; found, 601.114. *m/z*: calcd for $C_{28}H_{28}ClFeN_5O_2$, $[Fe^{III}(tpena)(m\text{-CBA})-CO_2]^+$, 557.128; found, 557.124. *m/z*: calcd for $C_{20}H_{22}FeN_5$, $[Fe^{II}(tpena)-CH_2COO]^+$, 388.122; found, 388.119. *m/z*: calcd for $C_{22}H_{26}ClFeN_{6}$, $\{[Fe^{II}(CI)(tpena)-CH_2COO](MeCN)\}^+$, 465.125; found, 465.075.

counterpart $[Fe(O-t-Bu)(tpenaH)]^{2+}$ and $[Fe(Ocumyl)-(tpenaH)]^{2+}$ complexes. This was verified by recording ESImass spectra of $[Fe(tpena)]^{2+}$ solutions in the presence of 50 equiv of *t*-BuOH or *m*-CBAH. Both show a base peak at m/z =446.1256 corresponding to $[Fe^{II}(tpena)]^+$; however, the spectrum of the mixture containing *m*-CBAH contains also two intense peaks at m/z = 601.114 (59%; calcd for

 $C_{29}H_{28}ClFeN_5O_4$, 601.117) and m/z = 557.124 (39%; calcd for C₂₈H₂₈ClFeN₅O₂, 557.128) which correspond to the *m*-CBA adduct ions, $[Fe^{III}(m-CBA)(tpena)]^+$ and $[Fe^{III}(m-CBA)(tpena)]^+$ $(CBA)(tpena) - CO_2^{\dagger}$, respectively (Figure 4c). These results show that the product *m*-CBAH inhibits step f in the catalytic cycle by formation of a relatively stable [Fe^{III}(OC(O)PhCl)-(tpenaH)²⁺ (Scheme 3). Commercial *m*-CPBA is significantly contaminated by *m*-CBAH, so this inhibitor is actually present from the first addition of its derived peroxide. Consistently with the ESI-MS, UV-vis and EPR spectra of acetonitrile solutions of $[Fe(tpena)]^{2+}$ are not affected by the addition of *t*-BuOH whereas the addition of m-CBAH results in the disappearance of the characteristic band of $[Fe(tpena)]^{2+}$ at $\lambda_{\text{max}} = 360 \text{ nm}$. The EPR spectrum of this latter solution reproduces the high-spin signal ($g^{\text{eff}} = 8.5, 5.2, 4.2, 3.0$) of the working solutions where *m*-CPBA is the substrate (Figure 4b; Figure S12). It is therefore unambiguous that the EPR signal can be assigned to high-spin (S = 5/2) [Fe^{III}(tpenaH)(m- $(CBA)^{2+}$

CONCLUSION

The Fe-tpena system, uniquely compared to all other known nonheme models, contains a chelating single carboxylato donor cis to the peroxide binding site. This is biomimetic with respect to the propensity of the occurrence of mono Asp/Glu coordination cis to O2 activating enzymatic nonheme sites. Transient low-spin iron(III)-alkylperoxides and iron(III)acylperoxides $[Fe^{III}OOR(tpenaH)]^{2+}$ (R = C(CH₃)₃, C- $(CH_3)_2$ Ph, C(O)PhCl) form on the replacement of the water equivalent in [Fe^{III}(OH)(tpenaH)]²⁺ by ROOH. The complex is bifunctional: The ingoing and outgoing coligands are charge separated into a XO^- (X = H, RO) ligand, and a proton on the noncoordinated pyridinium arm. This system is the first nonheme iron model incorporating a biomimetic second coordination sphere base for enabling this outcome. The $\nu_{\text{Fe}=0}$ for the derived $[\text{Fe}^{\text{IV}}O(\text{tpenaH})]^{2+}$ is hypsochromically shifted, by around 30 cm⁻¹, compared to the iron(IV)oxo complexes of N-donor-only aminopyridyl ligands.⁴⁴ The way in which these structural and electronic features are important for the indisputable inherent radical character of the unique [Fe^{IV}O(tpenaH)]²⁺¹¹ is yet to be determined; however, it is pertinent to note that carboxylato donors are redox noninnocent and this will influence the activation of the bonds to and in cis ligands. For example, the lability of the FeO-OR bond in the alkyl and acyl peroxide adducts of Fe-tpena is greater than that of analogous iron complexes supported by the more mundane N-donor-only ligands. These factors are intrinsic for the unified peroxidase-like mechanism we propose (Scheme 3). The speed of the reaction and the extensive characterization of the iron-based and organic species in our working solutions lead us to propose that the evolved O₂ predominantly derives from the O₂ extrusion from a putative Fe^{III}OOOR species obtained from coupling of the radical iron(IV)oxo complex with ROO[•].

With its resting-state +3 oxidation state and readily accessible +4 state the iron-tpena system is highly applicable to one-electron reactions in cycles, i.e., those involving HAT reactions as represented by the top section of Scheme 1 in the presence of peroxides as terminal oxidants. All the reactions described here support this conclusion. Interestingly, despite the presence of several radical species (ROO[•], RO[•], R[•], [Fe^{IV}O(tpenaH)]²⁺) in these reactions, with judicial exper-

imental design, the selective oxidation of an external substrate can be favored.

Ultimately, our results demonstrate that disproportionation of alkyl hydroperoxides and peroxyperacids can potentially be a significant background reaction, when these reagents are used as terminal oxidants in metal-catalyzed reactions. It is clear, however, given the number of applications of these reagents, including commercial, that significant unproductive decomposition of alkyl hydroperoxide is in fact relatively rare. Finally, as an effective catalyst for alkyl hydroperoxide disproportionation, $[Fe(tpena)]^{2+}$ might find useful application in quenching unwanted hydrogen alkyl peroxides in cases of excesses or in chemical spills.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b02882.

EPR, UV-vis, Mössbauer, and NMR spectra of reaction mixtures; MIMS data; and supporting plots for the volumetric experiments (PDF)

 O_2 evolution observed on *t*-BuOOH disproportionation (AVI)

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Notes

The authors declare no competing financial interest.

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