Oxidation of Iron(III) Tetramesitylporphyrin with Dimethyldioxirane

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The oxidation of (TMP)$Fe^{III}ClO_4$ in solution with dimethyldioxirane-d_6 has been examined by ^1H NMR spectroscopy. The reaction of (TMP)$Fe^{III}ClO_4$ with dimethyldioxirane-d_6 in a solvent mixture of dichloromethane-d_2/methanol-d_4 (4:1 v/v) produced two intermediates: (TMP)$Fe^{IV}(CD_3O)_2$ and X($TMP^\bullet$)$Fe^{IV}O$, which could be directly observed at low temperatures. When the (TMP)$Fe^{III}ClO_4$−dimethyldioxirane-d_6 reaction was carried out in dichloromethane-d_2, the loss of iron(III) tetramesitylporphyrin resonances was accompanied by growth of resonances due to (TMP)$Fe^{IV}(CD_3O)_2$ and X($TMP^\bullet$)$Fe^{IV}O$. A set of ferryl porphyrin cation radicals X($TMP^\bullet$)-$Fe^{IV}O$ (X − ligands available) was identified. The formation of a variety of ligands resulted from side reaction pathways which include dioxirane and dichloromethane-d_2. Addition of dimethyldioxirane-d_6 to the acetone-d_6 solution of (TMP)$Fe^{III}ClO_4$ gave mainly iron(III) porphyrin cation radical $[(TMP^\bullet)Fe^{III}((CD_3)_2CO)_2]^+$ and a small amount of ferryl porphyrin cation radicals $[(CD_3)_2CO(TMP^\bullet)Fe^{IV}O]^+$. Typically, in the (TMP)$Fe^{III}ClO_4$−dioxirane systems the formation of one-electron oxidation product (iron(IV) porphyrin or iron(III) porphyrin radical) predominates, rendering such an approach less effective in generation of green ferryl porphyrin cation radicals than use of iodozobenzene, peroxyacids, or ozone.

Introduction

Several pathways have been explored to generate ferryl(IV) iron porphyrin cation radicals ($P^\bullet$)$Fe^{IV}O$ since such species are considered to model the active state of P-450 monooxygenase or horseradish peroxidase and have been included as a fundamental active form into mechanisms of several iron porphyrin-based catalysts.[1,2] The oxidation of iron(III) complexes with sterically hindered porphyrins exemplified here by tetramesitylporphyrin ($TMPH_2$) with iodozobenzene, peroxyacids, or ozone resulted in generation and spectroscopic characterization of green ferryl(IV) iron porphyrin cation radicals ($P^\bullet$)$Fe^{IV}O$.[2−6] The independent route involved a formation of (TMP)Fe^{III}-$OOFe^{III}$(TMP), followed by its homolytic cleavage to produce (TMP)$Fe^{IV}O$, and finally by the chemical oxidation of (TMP)-$Fe^{IV}O$ to yield highly oxidized product $[(TMP^\bullet)Fe^{IV}O]^+$.[7,8] The electrochemical oxidation of (TMP)Fe^{III}(OH) or (TMP)$Fe^{IV}O$ was also explored.[9] The disproportionation of ($TMP^\bullet$)Fe^{III}-$(ClO_4)_2$ in the presence of 1 equiv of methoxide to produce (CH_3O)($TMP^\bullet$)$Fe^{IV}O$ was briefly reported.[3d] Groves et al. suggested a disproportionation of (TMP)$Fe^{IV}O$ to contribute to the major pathway for olefin oxidation although the existence of the ferryl porphyrin cation radical species in the system was not directly shown.[10] The formation of X($TMP^\bullet$)$Fe^{IV}O$ from ($TMP^\bullet$)$Fe^{III}(ClO_4)_2$ in the presence of 2,4,6-collidine (coll) has been recently determined[11] by ^1H NMR spectroscopy, according to the reaction

$$2X(TMP^\bullet)Fe^{III}(OH) + \text{coll} \rightarrow X(TMP^\bullet)Fe^{IV}O + (TMP)Fe^{III}(OH) + \text{collH}^+ + X^-$$

The availability of dioxiranes in solution opens a possibility to probe a new route to generate highly oxidized metalloporphyrins.[12] Dioxiranes are strong oxidants and oxygen atom transfer agents able to effectively epoxide alkenes and to insert the oxygen into C−H bonds. In solution dioxiranes undergo thermal autodecomposition to produce isomeric esters or products of ester hydrolysis.[13] Generally dioxiranes were

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reported to be unstable in the presence of transition metal ions (e.g. Fe^{II}, Mn^{II}) as they stimulate their decomposition.[14] This fact initiated some studies on formation of high-valent metal−oxo species by oxidation of carbonyl complexes of rhenium and molybdenum with dimethyldioxirane as well as on oxygen atom transfer to iron(II) porphyrins.[15] Since that time, metal complexes were used as catalysts for oxidation reactions with dioxiranes as the oxygen source.[16] Interestingly dioxiranes were successfully applied to oxidize ligands coordinated to transition metal ions.[17] Finally manganese(III) and iron(III) tetrarylporphyrins were used as catalysts in epoxidation of uracil derivatives with dimethyldioxirane.[18]

In these investigations we have explored the reactivity of dimethyldioxirane with respect to iron(III) tetramesitylporphyrin in search for a new route to generate the ferryl porphyrin cation radicals. To facilitate the detection of reaction products we have undertaken systematic ^1H NMR investigations of the (TMP)$Fe^{III}(ClO_4)$−dimethyldioxirane system, taking an advantage of the fact that this spectroscopy provides extremely useful probe for studying directly the structure and chemistry of paramagnetic iron porphyrins under such demanding experimental conditions. The hyperfine shift patterns of metalloporphyrins are particularly sensitive to the symmetry, spin/electronic, and ligation states.[19] Consequently, by carrying out the ^1H NMR experiment at low temperatures, we have detected highly oxidized intermediates formed during the process.

Results and Discussion

The reaction of (TMP)$Fe^{III}ClO_4$ (**1**) with dimethyldioxirane-d_6 in a solvent mixture of dichloromethane-d_2/methanol-d_4 (4:1 v/v) has been followed by ^1H NMR spectroscopy. The representative spectra are presented in Figure 1. The initially formed bis-methanol adduct [(TMP)$Fe^{III}(CD_3OD)_2$](ClO_4) (**1′**) demonstrates the characteristic ^1H NMR spectrum (203 K) typical for this type of ligation with the β-H pyrrole at 47.9 ppm and the meta phenyl at 11.84 ppm singlets, respectively (trace A, Figure 1).[20] Of particular significance is the observation of a single resonance for meta protons. This pattern is indicative of the symmetrical coordination with respect to the porphyrin plane. Addition of 10 equiv of dimethyldioxirane in acetone-d_6 at 203 K did not show sign of any reaction at a reasonable rate in our studies. However the increase of temperature to 213 K resulted in the markedly higher concentration of (TMP)$Fe^{III}Cl$ (**2**) within 15 min. Originally the sample contained only some traces of **2** that was present due to the incomplete methathesis of **2** into **1**. In the initial course of reaction the molar ratio of **2** to **1′** reached the value 1:2.6. Further warming to 223 K resulted in formation of a new species with a characteristic β-H pyrrole resonance at −30 ppm.[21] This form has been also unambiguously identified as (TMP)$Fe^{IV}(CD_3O)_2$ (**3**) in an independent experiment. Consequently [$(TMP^{\bullet})Fe^{III}$]$(ClO_4)_2$ (**4**) was dissolved in a solvent mixture of dichloromethane-d_2/methanol-d_4 (4:1 v/v). The spectrum of the resulting [$(TMP^{\bullet})Fe^{III}(CD_3OD)_2$]$(ClO_4)_2$ (**4′**) consists of pyrrole β-H 81.75, m-H 107.76, o-CH_3 36.11, and p-CH_3 24.62 ppm resonances at 213 K. The generated cation radical **4′** has been treated with sodium methoxide in methanol-d_4 to give **3** which presents the same spectrum as the product of the reaction with dioxirane shown in trace B of Figure 1. The ^1H NMR spectrum of **3** was previously analyzed and the component resonances were assigned.[21]

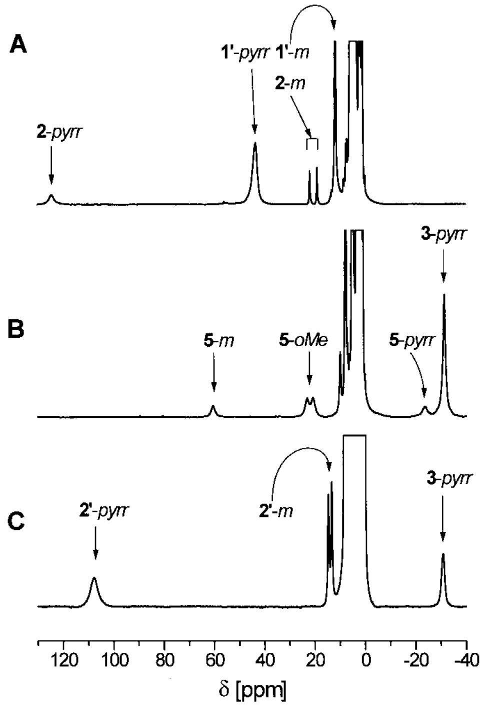

Figure 1. ^1H NMR spectra obtained for the solutions prepared in following experiments: (A) (TMP)$Fe^{III}ClO_4$ dissolved in dichloromethane-d_2/methanol-d_4 (4:1 v/v) after the addition of 10 equiv of dimethyldioxirane-d_6 in acetone-d_6, warmed to 213 K for 15 min, collected at 203 K; (B) same sample as in trace A at 223 K after brief warming to 233 K; (C) $(TMP^{\bullet +})Fe^{III}(ClO_4)_2$ cation radical dissolved in dichloromethane-d_2/methanol-d_4 (4:1 v/v) and treated with sodium methoxide at 196 K in methanol-d_4 to give (TMP)$Fe^{IV}(CD_3O)_2$ (spectrum collected at 223 K). Resonances from individual species are identified by **1**−**5** as defined in the text. Annotation denotes specific protons: pyrr, pyrrole protons; *m*, meta; *o*-Me, *ortho*-methyl.

Subsequently the reaction was examined at 233 K. The new product of oxidation has been formed and identified as [$(CD_3OD)(TMP^{\bullet})Fe^{IV}O$]$^+$ (**5**) by a diagnostic set of resonances (pyrrole β-H, −25.69; o-CH_3, 21.25, 22.45; p-CH_3, 10.76; m-H, 65.37 ppm; 213 K). The ^1H NMR spectrum of **5** measured at 213 K matched that one created by known procedures, i.e., oxidation of **1** with *m*-chloroperoxybenzoic acid in dichloromethane-d_2/methanol-d_4 (4:1 v/v). As the ^1H NMR spectra of ferryl porphyrin cation radicals are specially sensitive to the

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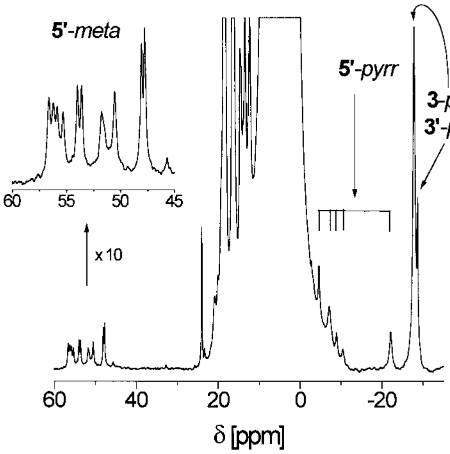

Figure 2. ^{1}H NMR spectrum of a dichloromethane-d_2 solution of (TMP)$Fe^{III}ClO_4$ at 243 K to which 10 equiv of dimethyldioxirane-d_6 in acetone-d_6 has been added. Resonances due to a set of X(TMP$^•$)-$Fe^{IV}O$ species has been labeled **5′**. Inset presents the details of the diagnostic meta proton region of the spectrum. Other peak assignments as in Figure 1 and in the text.

axial ligation we could identify an axial ligand of **5** as methanol-d_4.[3d,4,6,7] The species **5** was unstable in basic conditions; an addition of excess sodium methoxide resulted in immediate reduction of **5** into **3** even at 196 K. Upon standing at 233 K the peaks due to **3** increase its intensity and after 1 h the molar ratio of **3** to **5** reached ca. 9:1. Simultaneously the substrate **1′** has been completely consumed. Further increase of temperature resulted in the total decay of **5** to produce **2** or (TMP)Fe^{III}(OD) (**2′**) via abstraction of the deuterium atom from the solvent.[4a,10,22] As expected **3** was relatively more stable but decomposed eventually at 273 K within 1 h. It should be noted that addition of norbornene to the solution containing **5** and **3**, generated as described above, resulted in the immediate and selective reduction of **5** into **2** (**2′**) due the oxygen transfer to the organic substrate to produce norbornene oxide as typical for ferryl porphyrin cation radicals.[3a] The addition of 10 equiv of dimethyldioxirane-d_6 in acetone-d_6 to **2′** in dichloromethane-d_2/methanol-d_4 (4:1 v/v) at 203 K produced mainly **3** and only traces of **5** once the sample was warmed to 233 K.

More complicated results have been obtained when the **1**−dimethyldioxirane-d_6 reaction was carried out in dichloromethane-d_2 rather than dichloromethane-d_2/methanol-d_4. We have monitored this reaction at 243 K. Figure 2 gives the results of the representative experiment. The loss of iron(III) tetramesitylporphyrin resonances is accompanied by growth of resonances due to **3** and X(TMP$^•$)$Fe^{IV}O$ (labeled as **5′**). The concentration of **3** was markedly higher than the combined concentrations of other highly oxidized products. Actually a set of ferryl porphyrin cation radicals X(TMP$^•$)$Fe^{IV}O$ (X = ligands available) has been identified. The resonance assignments in Figure 2 have been based on relative intensities and comparison with spectra of analogous species generated in extensive studies on models of HRP compound **I**.[3−5,8,11] They do retain the spectral pattern of the ferryl porphyrin π cation radical although they are significantly different considering the chemical shift values. We attribute these shift changes to the axial ligand replacement although the identity of the particular ligand could not be here determined. However their presence points out for the more complicated, probably of the radical nature, reaction pathways which might include dioxirane-d_6 and dichloromethane-d_2. Accordingly the presence of **3** in the reaction products has been explained by the fact that methoxide-d_3 has been formed from dioxirane-d_6 in the course of the reaction. The identical species has been already detected when the reaction has been carried out in the presence of methanol-d_4. Although the excess of methanol-d_4 simplified the spectroscopic picture a source of the methoxide (methanol-d_4 vs dioxirane-d_6) could not be determined. Interestingly, our ^{1}H NMR results indicate that the other iron(IV) porphyrin products are formed as well. The additional resonance at −28.71 ppm, i.e., in the region typical for iron(IV) porphyrin alkoxides suggests the formation of other alcohol in the process (**3′**).

Finally, the effect of addition of dimethyldioxirane-d_6 to the acetone-d_6 solution of **1** has been examined at 213 K. The ferryl porphyrin cation radical [((CD$_3$)$_2$CO)(TMP$^•$)$Fe^{IV}O$]$^+$ (**5″**) (pyrrole H, −16.32; meta H, 65.00, 65.46 ppm at 213 K) has been detected as the minor reaction product. The iron(IV) porphyrin **3** has not been observed. Instead the one-electron oxidation route led to iron(III) porphyrin cation radical [(TMP$^•$)Fe^{III}((CD$_3$)$_2$CO)$_2$]$^+$ **4″** (pyrrole, 89.95; *m*-H, 107.47; *o*-CH$_3$, 37.21; *p*-CH$_3$, 24.10 ppm at 213 K) as the major reaction product. In the related experiment the identical species **4″** has been generated by addition of acetone-d_6 to the dichloromethane solution of **4**. It has been also found that the generation of **5** with dimethyldioxirane absolutely requires (TMP)Fe^{III}X as a substrate. Any attempts to oxidize **3**, **4**, or **4′** in appropriate solvents failed to generate **5**.

To complete the description of dioxirane reactivity in the presence of **1**, identification of selected feasible organic product has been accomplished by means of GC−MS. To avoid the side product formation all reactions have been carried out at 233 K. Thus treatment of **1** with dimethyldioxirane-d_6 in acetone-d_6 gave direct evidence by GC−MS of the formation of methanol-d_4 and methyl acetate-d_6. The identity of products was confirmed by injection of original compounds. Quantitative determination of products was very difficult due to the fact of their low concentration and similar mobility. However, the amount of methyl acetate-d_6 formed was approximately 3 times higher than the concentration of **1**. A variety of products have been observed when dichloromethane has been used as additional solvent. The sample revealed the presence of CH_3CH_2Cl, CH_3CH_2OH, CH_3CHO, CD_3OD listed according to the decreased concentration. The concentration of ethyl alcohol was ca. 5 times higher than the concentration of **1**. Additionally, some other chlorinated ethanes and ethenes were detected by GC−MS method due to dichloromethane conversion.

The observation recorded here indicates a consistent pattern of behavior of the iron(III) tetramesitylporphyrin upon addition of dimethyldioxirane-d_6. The formation of the detected iron porphyrin products in dichloromethane-d_2/methanol-d_4 can be accounted for by two parallel routes:

$$[(\mathrm{TMP})\mathrm{Fe}^{\mathrm{III}}(\mathrm{CD_3OD})_2]^+ + (\mathrm{CD_3})_2\mathrm{CO_2} \rightarrow [(\mathrm{CD_3OD})(\mathrm{TMP}^\bullet)\mathrm{Fe}^{\mathrm{IV}}\mathrm{O}]^+ + (\mathrm{CD_3})_2\mathrm{CO} + \mathrm{CD_3OD} \quad (1)$$

$$2[(\mathrm{TMP})\mathrm{Fe}^{\mathrm{III}}(\mathrm{CD_3OD})_2]^+ + (\mathrm{CD_3})_2\mathrm{CO_2} \rightarrow 2(\mathrm{TMP})\mathrm{Fe}^{\mathrm{IV}}(\mathrm{CD_3O})_2 + (\mathrm{CD_3})_2\mathrm{CO} + 2\mathrm{D}^+ + \mathrm{D_2O} \quad (2)$$

We have already demonstrated that **4** does not serve as a precursor of **5** under condition of our experiments. In dichloromethane-d_2 instead of methoxide-d_3 other anions, generated in the side reactions, compete for coordination to produce **5**.

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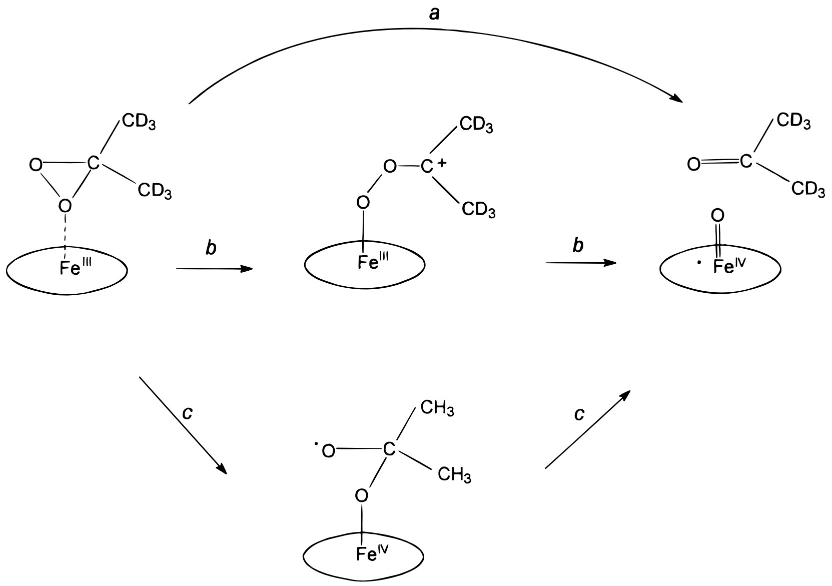
Scheme 1



The reaction, carried out in acetone-d_6, can be described as follows:

$$[(TMP)Fe^{III}((CD_3)_2CO)_2]^+ + (CD_3)_2CO_2 \rightarrow [((CD_3)_2CO)(TMP^{\bullet})Fe^{IV}O]^+ + 2(CD_3)_2CO \quad (3)$$

$$2[(TMP)Fe^{III}((CD_3)_2CO)_2] + (CD_3)_2CO_2 + 2D^+ \rightarrow 2[(TMP^{\bullet})Fe^{III}((CD_3)_2CO)_2]^{2+} + (CD_3)_2CO + D_2O \quad (4)$$

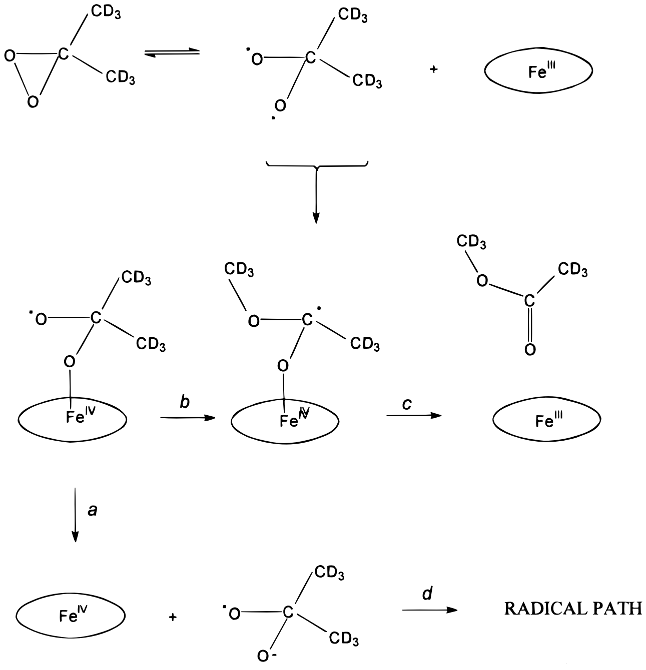
Details of how reactions 1−4 proceed deserve further comments and study. In the course of our investigations an intermediate preceding formation of any highly oxidized porphyrins has not been observed. However by analogy to widely investigated mechanisms of dioxirane reactivity with respect to organic substrates[12−18] and as well as to mechanisms of ferryl porphyrin radical formation,[3−11] the feasible routes, presented below in Schemes 1 and 2, can be considered.

Thus for the formation of ferryl porphyrin cation radicals (Scheme 1), the likely mechanisms include a concerted path with O−O and C−O breaking occurring (path *a*), via carbonyl oxides involving heterolytic (path *b*) or homolytic (path *c*) cleavage of the O−O bond) to give an oxidized ferryl complex at the peroxidase compound **I** level of oxidation and the molecule of acetone-d_6.

One-electron oxidation products of reactions 2 and 4 can be formed according to an independent pathway (Scheme 2), formally by reaction of bisoxymethylene diradical with iron(III) porphyrin followed by dissociation of the one-electron reduced dioxirane radical (path *a*). Strictly this mechanism corresponds to diradical mechanism discussed for epoxidation with dioxiranes in the metal ion absence.[12] The same intermediate may be instrumental in isomerization of dimethyldioxirane to methyl acetate at low temperature (paths *b* and *c*).

The isomerization of dioxiranes to corresponding esters was previously observed at 298 K and did not require any catalyst.[13] However under condition of our experiment, i.e., at 233 K the isomerization has been observed exclusively after addition of iron(III) porphyrin, suggesting its direct involvement in the process. The bisoxodimethylradical and other radicals formed in the course of the process might trigger the radical chain reactions (path *d*) with the chlorinated solvent accounting for a large variety of products determined by GC−MS experiment.

Scheme 2



In conclusion, this work offers the spectroscopic evidence that ferryl porphyrin cation radical can be formed in reaction of iron(III) tetramesitylporphyrin with dimethyldioxirane acting as an oxygen atom transfer reagent. However the competing reactions where dioxirane acts as one electron oxidizing reagent to produce iron(IV) porphyrin or iron(III) porphyrin radicals predominates, rendering this approach definitely less effective in generation of green ferryl porphyrin cation radicals as compared to previously established routes with peroxybenzoic acid, iodobenzene or ozone as oxidants.

Experimental Section

Tetramesitylporphyrin ($TMPH_2$) was prepared using reported methods.[23] Insertion of iron followed known routes.[24] $(TMP)Fe^{III}ClO_4$ was obtained (on a 3 mg scale) by neutralization of the (TMP)Fe^{III}(OH) dichloromethane solution[25] with aqueous $HClO_4$. ($TMP^{\bullet}$)$Fe^{III}$$(ClO_4)_2$ was synthesized according to described procedures.[26]

Dimethyldioxirane-*d*$_6$. The dimethyldioxirane-*d*$_6$ solution in acetone-*d*$_6$ was prepared from acetone-*d*$_6$ (Glaser AG Basel) and OXONE (Aldrich) according to the published procedure[27] on the small scale (5 mL of acetone-*d*$_6$) prior to use in ^{1}H NMR and GC−MS experiments. The concentration of dimethyldioxirane-*d*$_6$ as determined by iodometric titration was typically 0.15 M.

GC−MS Experiments. The organic products of reaction between (TMP)$Fe^{III}ClO_4$ with dimethyldioxirane in acetone-*d*$_6$ or acetone-*d*$_6$/dichloromethane were separated and identified using GC−MS. In a series of experiments the concentration of (TMP)$Fe^{III}ClO_4$ was kept at 2 mM. The concentration of dimethyldioxirane-*d*$_6$ was varied to obtain 50:1 and 10:1 molar ratios of dimethyldioxirane-*d*$_6$ to (TMP)$Fe^{III}ClO_4$. Typically the stock 0.15 M dimethyldioxirane-*d*$_6$ solution in acetone-*d*$_6$ was added to (TMP)$Fe^{III}ClO_4$ in acetone-*d*$_6$ or methylene dichloride at 200 K. The temperature was increased gradually with continuous stirring up to 233 K, and the reaction mixture was kept 2 h at this temperature protected against light. The organic products of reaction were then vacuum transferred (233 K) into a separate flask and subjected to GC−MS and GC.

Low-Temperature Reactivity Studies. The reactions between (TMP)$Fe^{III}ClO_4$ and dimethyldioxirane-*d*$_6$ were performed typically by injection of 100 μL of 0.15 M dimethyldioxirane-*d*$_6$ in acetone-*d*$_6$ into the 450 μL of 0.003 M (TMP)$Fe^{III}ClO_4$ in the appropriate solvent(s) in an NMR tube at 193 K. Thus, always at least 10-fold excess of the oxidant was used. The sample was shaken in a cold bath (193 K) and transferred to the precooled NMR probe, and the progress of the reaction was followed by ^{1}H NMR.

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker AMX 300 spectrometer. The GC−MS separation and identification of products was carried out using a PoraPLOT-Q column an HP 5890 II column coupled with an HP 5971 A mass spectrometer.

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