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21-Telluraporphyrins. 2. Catalysts for Bromination Reactions with Hydrogen Peroxide and Sodium Bromide

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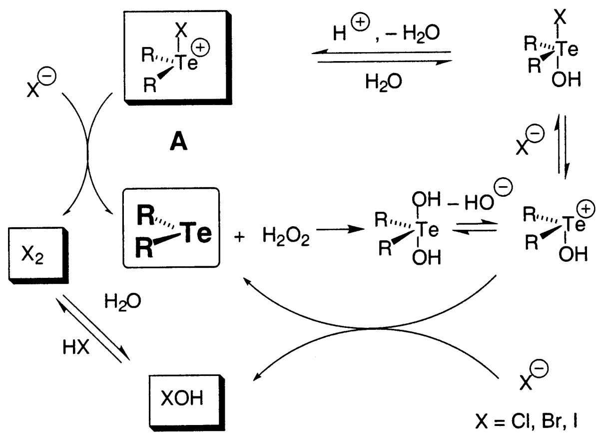
meso-Tetraphenyl-21-telluraporphyrins **3** and **4** act as catalysts for bromination reactions with H_2O_2 and NaBr. Oxidation of telluraporphyrin **3** with excess H_2O_2 follows pseudo-first-order kinetics with a second-order rate constant of 0.85 ± 0.02 M^{-1} s^{-1} at 20.5 °C in 1:1 CH_2Cl_2/ethanol. Bromination of 4-pentenoic acid in two-phase mixtures of CH_2Cl_2 and pH 6 phosphate buffer with a stoichiometric amount of NaBr in the presence of a 50% excess of H_2O_2 follows second-order kinetics as monitored by the loss of 4-pentenoic acid. Reactions of 4-pentenoic acid and 1,3,5-trimethoxybenzene with excess H_2O_2 and excess NaBr follow pseudo-first-order kinetics and are pseudo-first-order in bromide in two-phase mixtures. Brominations of 4-pentenoic acid were conducted with initial concentrations of 0.2 M 4-pentenoic acid, 1.5 M H_2O_2, and 1.0 M in NaBr in a two-phase system of CH_2Cl_2 and pH 6 phosphate buffer. Brominations of 1,3,5-trimethoxybenzene were conducted with initial concentrations of 0.2 M 1,3,5-trimethoxybenzene, 2.5 M H_2O_2, and 1.8 M in NaBr in a two-phase system of CH_2Cl_2 and pH 6 phosphate buffer. For both systems, telluraporphyrins **3** and **4** were added as catalysts at 0.2 mol % of substrate. Values of k_{cat} for **3** were $(4.0 \pm 0.1) \times 10^{-2}$ M^{-2} s^{-1} for bromination of 4-pentenoic acid and $(3.4 \pm 0.2) \times 10^{-2}$ M^{-2} s^{-1} for bromination of 1,3,5-trimethoxybenzene. Turnover numbers for **3** were ≥2000 for bromination of 4-pentenoic acid.

Organotellurides are catalysts for the activation of H_2O_2 in several reactions, perhaps the most useful of which is the conversion of halide salts to positive halogen sources.[1] Mechanistic studies have demonstrated two scenarios are plausible, as illustrated in Scheme 1. In both, initial oxidation of the organotelluride with H_2O_2 gives the +4 oxidation state of the telluride as a diorgano dihydroxy tellurane. Subsequent nucleophilic attack of a halide anion at the hydroxy ligand leads to reductive elimination to regenerate the organotelluride and the direct formation of the corresponding hypohalous acid in one scenario. In the other, initial oxidation with H_2O_2 is followed sequentially by ligand exchange and reductive elimination of the oxidized species with regeneration of the organotelluride, which can then reenter the catalytic cycle.[1c,d]

Scheme 1



The positive halogen species can be captured by organic substrates to give halogenation reactions. Product studies suggest not only that free halogen and hypohalous acid function as halogenating agents but also that the intermediate halotelluronium species (**A** in Scheme 1) can function as a halogenating agent.[1,2]

The strength of the Te−X bond also impacts the catalytic cycle. The ease of oxidation is $I^- > Br^- > Cl^-$, with F^- unreactive under all conditions examined to date, and the rates of halogenation of organic substrates also parallel this order.[1,2] In stoichiometric reactions, selenium(IV) bromides were found to be better brominating agents than tellurium(IV) bromides presumably due to the weaker Se−Br bond strength, which facilitates bromine transfer.[3]

One approach to more active catalysts places an electronegative heteroatom in a position to function as a chelating ligand to the oxidized tellurium center as illustrated in Scheme 2 for organotellurides **1** and **2**.[1d−f]

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Scheme 2

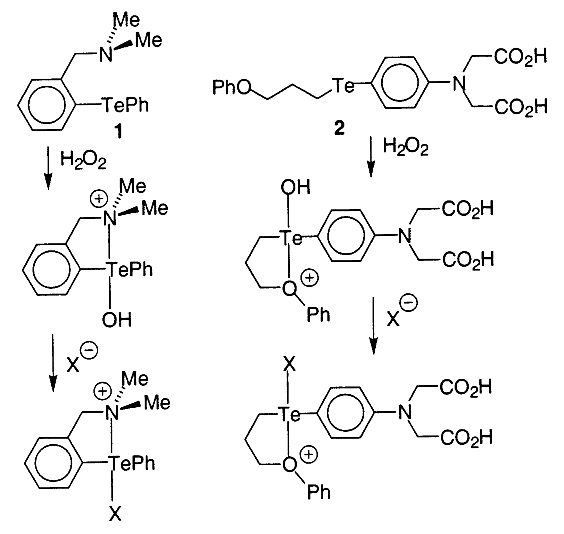
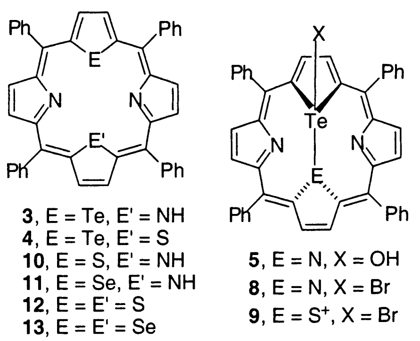


Chart 1



3, E = Te, E' = NH
4, E = Te, E' = S
10, E = S, E' = NH
11, E = Se, E' = NH
12, E = E' = S
13, E = E' = Se

5, E = N, X = OH
8, E = N, X = Br
9, E = S$^+$, X = Br

The chelating heteroatom helps stabilize both the initial hydroxy telluronium intermediate and the halotelluronium intermediate from ligand exchange through the formation of trigonal bipyramidal Te(IV) (equatorial lone pairs of electrons omitted for clarity in Scheme 2).[3] The chelating ligand prevents the intermolecular addition of a second ligand to the oxidized tellurium atom, while the positive charge activates oxidation of the attached ligand through nucleophilic attack.[1e,3]

21-Telluraporphyrin **3** and 21-tellura-23-thiaporphyrin **4** (Chart 1) have properties that suggest utility as catalysts for the activation of hydrogen peroxide.[4-6] These molecules are more readily oxidized than core-modified porphyrins containing only lighter chalcogen atoms as determined by electrochemical oxidation potentials[4] and products from air oxidation.[4,5] The intramolecular 21,23-heteroatom contacts are less than the sum of van der Waals radii: 3.13 Å for Te···N distances in a closely related analogue of **3**[5] and 2.65 Å for Te···S distances in **4**.[6] Thus, 21-tellurium-23-heteroatom contact is enforced, which should facilitate donation of a pair of electrons from the 23-heteroatom to the more electropositive tellurium atom as it is oxidized and should stabilize Te(IV) intermediates once they are formed. The porphyrin ring has preorganized the 23-heteroatom to interact with the 21-tellurium atom. Herein, we demonstrate that 21-telluraporphyrins are catalysts for the activation of H_2O_2 in bromination reactions of organic substrates with H_2O_2 and NaBr.

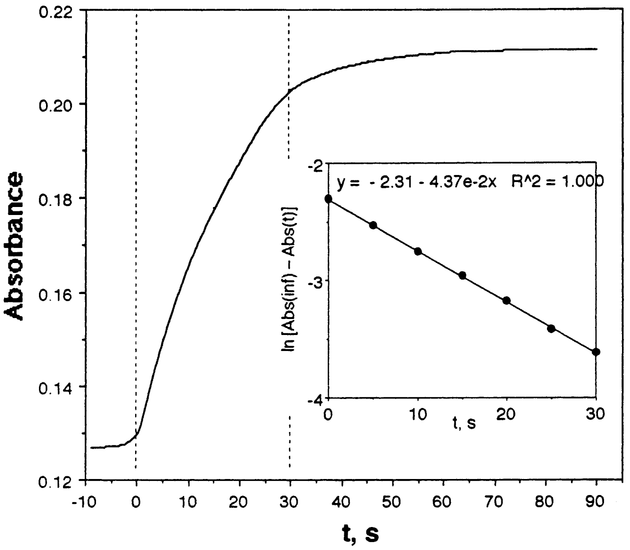


Figure 1. Oxidation of 21-telluraporphyrin **3** (5×10^{-5} M) with H_2O_2 (0.05 M) in 1:1 ethanol/CH_2Cl_2 at 20.5 (±0.5) °C as monitored by time-drive spectroscopy at 680 nm. Data between 0 and 30 s are plotted as the natural logarithm of the absorbance at infinity [Abs(inf)] minus the natural logarithm of the absorbance at time "*t*" [Abs(*t*)] vs time (inset). The inset line represents the "least-squares" fit of the data.

Results and Discussion

Oxidation of 21-Telluraporphyrin 3 with H_2O_2. The catalytic reactions of organotellurides with H_2O_2 and halide salts have typically been conducted as two-phase systems with an organic phase of CH_2Cl_2, cyclohexane, or ether and an aqueous phase of a buffered system containing H_2O_2 and sodium halide.[1] 21-Telluraporphyrin **3** is oxidized by H_2O_2 in $CDCl_3$ to give 21-oxo-21-telluraporphyrin **5**[4,5] (Chart 1) as the only product. The proton transfer from the 23-NH group to the oxidized tellurium leads to a "neutral" Te(IV) derivative **5** with two electronegative ligands on Te(IV).

Earlier studies of the oxidation of **3** with H_2O_2 in EtOH indicated that the oxidation was rapid and the second-order rate constant was estimated to be ≥ 20 M^{-1} s^{-1}. A quantitative determination of the rate of oxidation of 21-telluraporphyrin **3**[4] with H_2O_2 was made in a one-to-one solution of ethanol and CH_2Cl_2, a solvent system in which the kinetics of oxidation were somewhat slower, at 20.5 (±0.5) °C. An aliquot of 30% H_2O_2 was added to a 5×10^{-5} M solution of **3** to give a final concentration of 0.05 M H_2O_2. As shown in Figure 1, the rate of oxidation was followed by the increase in absorption at 680 nm to give 21-oxo-telluraporphyrin **5**.[4,5] The oxidation demonstrated excellent pseudo-first-order kinetics (Figure 1, inset), from which the second-order rate for oxidation of **3** with H_2O_2 was determined to be 0.85 ± 0.02 M^{-1} s^{-1}.

Bromination of 4-Pentenoic Acid with H_2O_2 and NaBr. To determine the products of bromination of 4-pentenoic acid, Br_2 was added to 4-pentenoic acid in a two-phase system of CH_2Cl_2 and pH 6 phosphate buffer (0.5 N in phosphate). The two-phase system was

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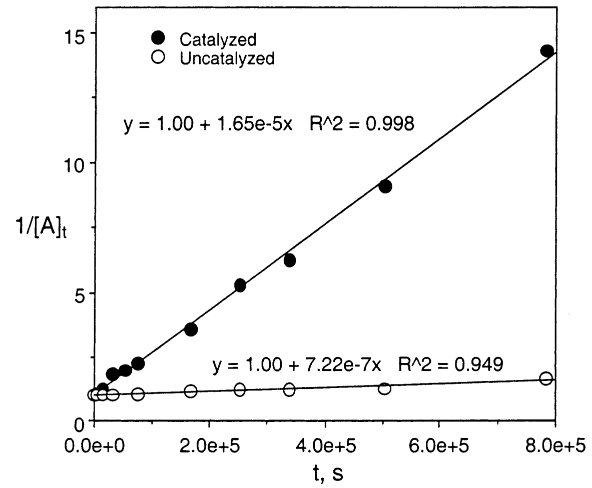
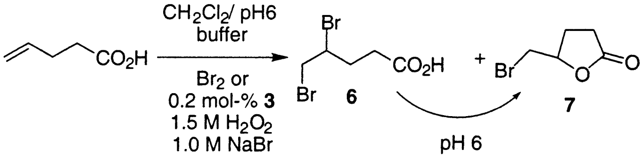


Figure 2. Rate of bromination of 4-pentenoic acid as a second-order kinetic plot for both the uncatalyzed reaction and the reaction catalyzed with 0.2 mol % telluraporphyrin **3** (4×10^{-4} M). Initial reaction conditions were 2.0 mmol of 4-pentenoic acid in 10 mL of CH_2Cl_2 and 2.0 mL of pH 6 phosphate buffer with 1.5 M H_2O_2 and 1.0 M NaBr. $[A]_t$ represents the concentration of 4-pentenoic acid at time "*t*". The lines represent the "least-squares" fit of the data.

Scheme 3



chosen since both 21-telluraporphyrin **3** and its oxidation product **5** have negligible aqueous solubility as determined spectrophotometrically and an organic phase would be necessary to conduct the catalytic reaction. Two products were observed: 4,5-dibromopentanoic acid **6** and bromolactone **7** (Scheme 3). Upon continued stirring in the two-phase system, all of dibromide **6** is converted to bromolactone **7**, which can be isolated in ≥90% yield.

As a control reaction, the bromination of 4-pentenoic acid with H_2O_2 and NaBr was conducted. A solution of 2.0 mmol of 4-pentenoic acid in 10 mL of CH_2Cl_2 was stirred with an aqueous phase of 2 mL of pH 6 phosphate buffer (0.5 N in phosphate) that was 1.5 M in H_2O_2 (3.0 mmol) and 1.0 M in NaBr (2.0 mmol). The rate of reaction, as well as product ratios of **6** and **7** and unreacted 4-pentenoic acid, was determined by periodic sampling of aliquots of the reaction mixture by ^1H NMR. At 27.0 (±0.5) °C, the second-order rate constant for bromination was measured as $(7.2 \pm 0.4) \times 10^{-7}$ M^{-1} s^{-1} (Figure 2).

Catalyzed Bromination of 4-Pentenoic Acid with 21-Telluraporphyrin 3. The addition of 0.2 mol % (relative to 4-pentenoic acid) of telluraporphyrin **3** greatly accelerated the reaction. As before, 2.0 mmol of 4-pentenoic acid as a 0.2 M solution in CH_2Cl_2 was stirred with an aqueous phase of 2 mL of pH 6 phosphate buffer (0.5 N in phosphate) that was 1.5 M in H_2O_2 and 1.0 M in NaBr. Under these conditions, equivalent molar quantities of 4-pentenoic acid and bromide were present. To this mixture was added 4 μmol of telluraporphyrin **3** (4×10^{-4} M in CH_2Cl_2).

Scheme 4

$$\mathrm{Br^-} + \mathrm{H_2O_2} \longrightarrow \text{"Br}^{+}\text{"} + 2\,\mathrm{HO^-} \qquad (1)$$

$$\text{"Br}^{+}\text{"} + \mathrm{H_2O_2} \longrightarrow \mathrm{Br^-} + \mathrm{O_2} + 2\,\mathrm{H^+} \qquad (2)$$

$$2\,\mathrm{H_2O_2} \longrightarrow \mathrm{O_2} + 2\,\mathrm{H_2O} \qquad (3)$$

$$\mathbf{6} + \mathbf{7} \xleftarrow{\text{4-pentenoic acid}} \text{"Br}^{+}\text{"} \xrightarrow{\mathrm{H_2O_2}} \mathrm{HBr} + \mathrm{O_2} + \mathrm{H^+}$$

Product ratios as well as relative amounts of unreacted 4-pentenoic acid were determined by periodic sampling of aliquots of the reaction mixture by ^1H NMR. As shown in Figure 2, the observed second-order rate constant was $(1.65 \pm 0.05) \times 10^{-5}$ M^{-1} s^{-1}, which represents a 23-fold increase in the rate of reaction relative to the uncatalyzed reaction (Figure 2). The rate acceleration corresponds to a rate constant for catalysis, k_{cat}, of $(4.0 \pm 0.1) \times 10^{-2}$ M^{-2} s^{-1} following correction for the uncatalyzed background reaction. With respect to product formation, comparable amounts of **6** and **7** are formed initially as shown in Figure S1 (Supporting Information), but the concentration of **6** reaches a maximum near 20−25% reaction and then decreases as **6** is converted to **7** with time.

Oxidation of bromide with H_2O_2 is also accompanied by decomposition of H_2O_2. While bromide is oxidized to "Br^+" by H_2O_2 as shown in eq 1 of Scheme 4, "Br^+" reacts with H_2O_2 to produce HBr, O_2, and a proton, as shown in eq 2 of Scheme 4.[7] The net reaction is the disproportionation of H_2O_2 with either bromide or "Br^+" as a catalyst (eq 3, Scheme 4). Thus, in competition with the addition of a "Br^+" source to 4-pentenoic acid is the disproportionation of H_2O_2 from reaction with some form of "Br^+". In the catalyzed bromination of 4-pentenoic acid, the reaction was stopped after 93% completion, which suggests minimal decomposition of H_2O_2 during reaction. The reaction of 2.0 mmol of 4-pentenoic acid, 3.0 mmol of H_2O_2, and 2.0 mmol of NaBr in the presence of 4 μmol of telluraporphyrin catalyst **3** represents >450 turnovers of catalyst for bromination of 4-pentenoic acid as shown in Figure S1.

After 450 turnovers, catalyst **3** retained its catalytic activity. We repeated the reaction under pseudo-first-order conditions to provide a more convenient time frame for monitoring the reaction with 2.0 mmol of 4-pentenoic acid in 10 mL of CH_2Cl_2, 17.6 mmol of H_2O_2, and 12.6 mmol of NaBr in 12 mL of pH 6 phosphate buffer and 4 μmol of telluraporphyrin catalyst **3**. Under the pseudo-first-order conditions, the half-life of the catalyzed reaction is approximately 2 h, while the half-life of the uncatalyzed reaction is roughly 80 h (Figure 3). The product distribution is unaffected by the pseudo-first-order conditions, as comparable amounts of **6** and **7** are formed initially as shown in Figure S2 (Supporting Information), but the concentration of **6** reaches a maximum near 50% reaction as **6** is converted to **7**.

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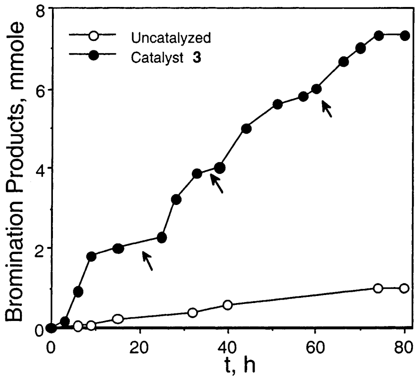

Figure 3. Catalytic activity of telluraporphyrin **3** through several cycles of substrate, H_2O_2, and NaBr. At time 0, 2.0 mmol of 4-pentenoic acid and 3.0 mg (4 μmol) of telluraporphyrin **3** in CH_2Cl_2 (10 mL) were added to pH 6 phosphate buffer (14 mL) with 1.0 M NaBr and 1.5 M H_2O_2. The reaction mixture was stirred at 27.0 (±0.5) °C. At the time points indicated by the arrows, an additional 2.0 mmol of 4-pentenoic acid, H_2O_2, and NaBr (to replace reagents consumed in the bromination) were added to the reaction mixture. Aliquots of the reaction mixture were sampled by ^1H NMR to determine relative amounts of unreacted 4-pentenoic acid and products **6** and **7**.

As shown in Figure 3, the reaction mixture for the catalyzed reaction was recharged with 2 mmol of 4-pentenoic acid, 2 mmol of H_2O_2, and 2 mmol of NaBr (to replace reagents consumed in the bromination) an additional three times. The data in Figure 3 correspond to approximately 2000 turnovers of catalyst **3** for bromination of 4-pentenoic acid. The apparent slowing of the reaction for the last two additions is most likely the result of decomposition of H_2O_2 during the course of reaction since the catalyst is unchanged spectroscopically.

Catalyzed Bromination of 4-Pentenoic Acid with 21-Tellura-23-thiaporphyrin 4. 21-Tellura-23-thiaporphyrin **4** also catalyzed the bromination of 4-pentenoic acid. However, compound **4** was much less efficient as a catalyst than **3**. At 0.2 mol % **4** under the pseudo-first-order conditions described above, the initial rate of bromination of 4-pentenoic acid corresponded to a half-life of ~13 h. However, the catalyzed reaction stopped after 400 turnovers of **4** for bromination of 4-pentenoic acid. Recharging the reaction with 2 mmol of 4-pentenoic acid, 2 mmol of H_2O_2, and 2 mmol of NaBr gave bromination at the much slower uncatalyzed rate. 21-Tellura-23-thiaporphyrin **4** could no longer be identified in the reaction mixture.

The product ratios were quite different during the course of reaction for the two catalysts. After two half-lives, the ratio of 4,5-dibromopentanoic acid **6** to bromolactone **7** was 20:80 using **3** as a catalyst. With **4** as a catalyst, the ratio of **6**:**7** was 70:30 after two half-lives. While sources of free "Br^+" might be common to the two reactions, bromotelluronium intermediates **8** and **9** (Chart 1) from **3** and **4**, respectively, may be responsible for the differences in product distribution through different Te−Br bond strengths as well as catalyst-specific side reactions.

Oxidative Addition of Bromine to Telluraporphyrin 3. In the catalytic cycle, bromotelluronium intermediate **8** would be formed by ligand exchange of bromide for the hydroxide ligand of **5**. Alternatively, **8** might be prepared by the direct oxidative addition of bromine to **3**. We attempted to prepare **8** from the slow addition of a slight excess of bromine to a solution of **3** in dry CH_2Cl_2. An immediate color change to a dark green solution was observed that turned red as more bromine was added. Upon standing, small black crystals of **8** formed that were isolated by filtration. The high-resolution electrospray mass spectrum of **8** gave *m*/*z* 808.0604, which is consistent with a molecular formula of $C_{44}H_{28}79BrN_3O^{130}Te + H^+$ (calc *m*/*z* of 808.0607) and oxidative addition of "Br^+" to the tellurium atom of **3**. Unfortunately, we have been unable to grow crystals suitable for X-ray crystallography.

The ^1H NMR spectrum of **8** resembled that of **5** and was consistent with oxidative addition of bromine and not electrophilic bromination of either a phenyl substituent or the porphyrin ring. The ^1H NMR spectrum consisted of a two-proton singlet at δ 10.45 corresponding to the two tellurophene ring protons, an AB pattern for four of the pyrrole ring protons at δ 8.48 and 8.43 with $J_{AB} = 4.3$ Hz, and a broadened singlet for two pyrrole ring protons at δ 8.35 at 21.5 °C. There are three distinct signals at δ 8.22, 8.17, and 8.10 in a 4:2:2 ratio for the *ortho*-phenyl protons ("doublet" structure) and several overlapping patterns between δ 7.9 and 7.6 for the *meta*- and *para*-protons of the *meso*-phenyl substituents. As with **5**,[4] the ^1H NMR signals for the aromatic protons of **8** are consistent with hindered rotation of the phenyl substituents. No signal for the N-*H* proton was detected by ^1H NMR, which is also consistent with the structure **8**.

Other 21- and 21,23-Core-Modified Porphyrins as Catalysts for Brominations with H_2O_2 and NaBr. Neither 21-thiaporphyrin **10** nor 21-selenaporphyrin **11** displayed catalytic activity in the bromination of 4-pentenoic acid with H_2O_2 and NaBr. The addition of 5 mol % of either **10** or **11** gave no increase in the observed rate of bromination of 4-pentenoic acid relative to the control, uncatalyzed reaction under the pseudo-first-order conditions described above. Similarly, the addition of 5 mol % of either 21,23-dithiaporphyrin **12** or 21,23-diselenaporphyrin **13** had no effect on the rate of bromination of 4-pentenoic acid with H_2O_2 and NaBr. When the core-modified porphyrins **10**−**13** were treated with 0.05 M H_2O_2 in pH 6 phosphate buffer, no new chromophores were formed. Instead, a slow bleaching of the core-modified porphyrin spectrum was observed. The products of this bleaching reaction were not determined. Only the 21-telluraporphyrin analogues **3** and **4** are oxidized by H_2O_2 to products that oxidize Br^- to "Br^+".

Bromination of 1,3,5-Trimethoxybenzene with H_2O_2 and NaBr. Bromination of 4-pentenoic acid involves formation of a bromonium ion intermediate via addition of "Br^+" to the C−C π-bond followed by inter- or intramolecular capture of a nucleophile. In the catalyzed reactions, the actual brominating agent may be a Te(IV) derivative such as **8** or **9** as well as a "free" source of "Br^+". In other bromination reactions, such as bromination of an aromatic substrate, the actual brominating agent may not result from the initial reaction, but may arise from the reversibility of brominated

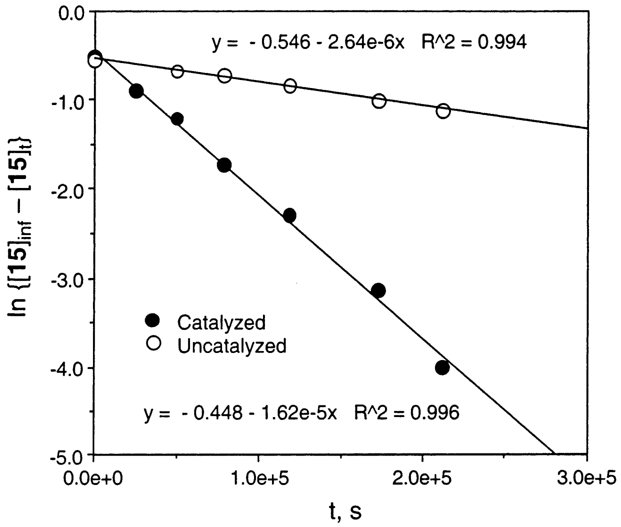

Figure 4. Formation of 2-bromo-1,3,5-trimethoxybenzene (**15**) during the time course of bromination of a two-phase mixture of 1,3,5-trimethoxybenzene (**14**, 2.0 mmol in 10 mL of CH_2Cl_2) and 14 mL of pH 6 phosphate buffer with 2.5 M H_2O_2 and 1.8 M NaBr with and without 0.2 mol % telluraporphyrin **3** (4×10^{-4} M) as a catalyst. The lines represent the "least-squares" fit of the data for formation of **15**.

intermediates. Thus, the catalyzed brominations of olefins and aromatic substrates may follow different courses.

The addition of 0.2 mol % of telluraporphyrin catalyst **3** (relative to substrate) accelerated the bromination of 1,3,5-trimethoxybenzene (**14**) to give 1-bromo-2,4,6-trimethoxybenzene (**15**) as shown in Figure 4. The uncatalyzed bromination of **14** (2.0 mmol in 10 mL of CH_2Cl_2) at 27.0 (±0.5) °C as a two-phase mixture of CH_2Cl_2 and pH 6 phosphate buffer (14 mL) with 2.5 M H_2O_2 (35 mmol) and 1.8 M NaBr (25 mmol) gave a pseudo-first-order rate constant of $(2.6 \pm 0.2) \times 10^{-6}\ s^{-1}$, while the addition of 0.2 mol % **3** gave a pseudo-first-order rate constant of $(1.6 \pm 0.2) \times 10^{-5}\ s^{-1}$ (Figure 4). This corresponds to a value of k_{cat} of $(3.4 \pm 0.4) \times 10^{-2}\ M^{-2}\ s^{-1}$ for the bromination of 1,3,5-trimethoxybenzene. For the catalyzed bromination of **14**, 285 turnovers of catalyst **3** were observed with respect to bromination and 8800 turnovers of catalyst with respect to decomposition of H_2O_2 (corresponding to 3.2% capture of "Br^+" in the catalyzed process). In this particular reaction, the decomposition of H_2O_2 by "Br^+", generated directly via reductive elimination from the catalyst or indirectly through the reversibility of the formation of intermediates, is the major pathway observed in the reaction. In the uncatalyzed process, approximately 3% of "Br^+" was also captured by **14** as a substrate.

Summary and Conclusions

21-Telluraporphyrins are unique among the 21- and 21,23-core-modified porphyrins with respect to catalytic activation of H_2O_2. Oxidation of the tellurium atom in these molecules with H_2O_2 is assisted by the heteroatom in the 23-position, which can also stabilize other telluronium intermediates. Reductive elimination at Te(IV) completes the catalytic cycle to regenerate the telluraporphyrin. Values of k_{cat} for telluraporphyrin **3** are large: $4.0 \times 10^{-2}\ M^{-2}\ s^{-1}$ for bromination of 4-pentenoic acid and $3.4 \times 10^{-2}\ M^{-2}\ s^{-1}$ for the bromination 1,3,5-trimethoxybenzene.

We have previously demonstrated that water solubility greatly improves catalyst performance.[1d] We are currently preparing water-soluble analogues of catalysts **3** and **4** as well as analogues in which the tellurophene is more electron rich for easier oxidation.

Experimental Section

General Methods. Solvents and reagents were used as received from Sigma-Aldrich Chemical Co (St. Louis, MO) unless otherwise noted. Concentration in vacuo was performed on a Büchi rotary evaporator. NMR spectra were recorded at 30.0 °C on a Varian Gemini-300, Inova 400, or Inova 500 instrument with residual solvent signal as internal standard: $CDCl_3$ (δ 7.26 for proton, δ 77.0 for carbon). Infrared spectra were recorded on a Perkin-Elmer FT-IR instrument. UV−visible−near-IR spectra were recorded on a Perkin-Elmer Lambda 12 spectrophotometer equipped with a circulating constant-temperature bath for the sample chambers. Elemental analyses were conducted by Atlantic Microlabs, Inc. High-resolution Q-TOF mass spectrometry was conducted by the Campus Chemical Instrumentation Center of The Ohio State University (Columbus, OH). Compounds **3**, **4**, and **10**−**13** were prepared as described in ref 4.

Oxidation of 21-Telluraporphyrin 3 with Hydrogen Peroxide. A 3.0 mL aliquot of a 5×10^{-5} M solution of **3** in 1:1 (v/v) ethanol/CH_2Cl_2 was placed in a quartz cuvette at 20.5 (±0.5) °C. A 17 μL aliquot of 30% (8.8 M) H_2O_2 was added, and the resulting solution was rapidly mixed to give a final concentration of 0.05 M H_2O_2. The kinetics of oxidation were followed by time-drive spectroscopy at 680 nm. The 680 nm wavelength was chosen in order to minimize the absorbance from **3** as the absorbance from **5** increased. Reactions were complete within 90 s. The observed rate constants were determined from the first 30 s following mixing. The reported rate constant of $0.85 \pm 0.02\ M^{-1}\ s^{-1}$ represents the average of triplicate runs.

General Procedure for Bromination of 4-Pentenoic Acid. A. Second-Order Conditions. 4-Pentenoic acid (0.20 g, 2.00 mmol) and catalyst **3** (3.0 mg, 4.0 μmol) were dissolved in a stirred mixture of 10 mL of CH_2Cl_2 and 2 mL of pH 6 phosphate buffer in a vessel contained in a 27.0 (±0.5) °C water bath. Sodium bromide (0.21 g, 2.0 mmol) and H_2O_2 (0.34 mL of a 30% (8.8 M) solution, 3.0 mmol) were added, and the resulting mixtures were stirred in the water bath at 27.0 (±0.5) °C until reaction was complete. In the uncatalyzed reactions, the reagents and concentrations were the same, but no catalyst was added. Aliquots of the reaction were monitored by ^1H NMR. Reactions were run in triplicate, and error limits are reported as the standard error from the mean.

B. Pseudo-First-Order Conditions. 4-Pentenoic acid (0.20 g, 2.00 mmol) and catalyst (3.0 mg for **3** or **4**, 4.0 μmol) were dissolved in a stirred mixture of 10 mL of CH_2Cl_2 and 10 mL of pH 6 phosphate buffer in a vessel contained in a 27.0 (±0.5) °C water bath. Sodium bromide (1.30 g, 12.6 mmol) and H_2O_2 (2.0 mL of a 30% (8.8 M) solution, 17.6 mmol) were added, and the resulting mixtures were stirred in the water bath at 27.0 (±0.5) °C until reaction was complete. In the uncatalyzed reactions, the reagents and concentrations were the same, but no catalyst was added. Aliquots of the reaction were monitored by ^1H NMR. When reaction was complete, the organic phase was separated and the aqueous layer extracted with two additional 5 mL aliquots of CH_2Cl_2. The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. Compounds **6** and **7** were separated by chromatography on SiO_2 eluted with hexanes−EtOAc (start at 5% EtOAc and manually increase to 20%). For one reaction in which the product mixture was allowed to stand until conversion of **6** to **7** was complete, workup gave 0.34 g (94%) of **7** from the reaction catalyzed by **3**:[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.69 (m, 1 H), 3.51 (m, 2 H), 2.39−2.68 (m, 2 H), 2.38 (m, 1 H), 2.08 (m, 1 H); IR (NaCl plate, film) 1780 cm^{-1} (C═O); *m*/*z* 178 ($C_5H_7{}^{79}BrO_2$).

For 4,5-dibromopentanoic acid **6**:[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.21 (m, 1 H), 3.85 (d×d, 1 H, $J = 4$, 10 Hz), 3.61 (d×d, 1 H, $J = 9$, 10 Hz), 2.45−2.68 (m, 3 H), 2.03 (m, 1 H); IR (NaCl plate, film) 3050 (br), 1711 cm^{-1} (C═O); FDMS, *m*/*z* 258 ($C_5H_8{}^{79}Br_2O_2$).

Bromination of 1,3,5-Trimethoxybenzene (14). Two reaction mixtures were prepared by dissolving 1,3,5-trimethoxybenzene (**14**, 0.336 g, 2.00 mmol) in a stirred mixture of 10 mL of CH_2Cl_2 and 10 mL of pH 6 phosphate buffer in vessels contained in a 27.0 (±0.5) °C water bath. To one mixture was added catalyst **3** (3.0 mg, 4.0 μmol). Sodium bromide (2.60 g, 25.2 mmol) and H_2O_2 (4.0 mL of a 30% (8.8 M) solution, 35.2 mmol) were added, and the resulting mixtures were stirred in the water bath at 27.0 (±0.5) °C until reaction was complete. Aliquots of each reaction were monitored by ^{1}H NMR. When reaction was complete, the organic phase was separated and the aqueous layer extracted with two additional 5 mL aliquots of dichloromethane. The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. The crude product mixture was dissolved in 5 mL of hexanes and chilled. The 2-bromo-1,3,5-trimethoxybenzene (**15**) was collected by filtration, and the crystals were washed with small portions of cold hexanes and dried: mp 91−93 °C (lit. mp[2] 91−93 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.16 (s, 2 H), 3.86 (s, 6 H), 3.80 (s, 3 H); FDMS, *m*/*z* 246 ($C_9H_{11}{}^{79}BrO_3$).

Oxidative Additon of Bromine to 3. A solution of bromine (80 mg, 0.5 mmol) in 2 mL of CH_2Cl_2 was added slowly to a solution of **3** (73 mg, 0.10 mmol) in 5 mL of CH_2Cl_2. The initial addition of bromine gave a green solution that became red upon further addition of bromine. After addition was complete, the reaction mixture was allowed to stand for 48 h. Small black crystals formed that were identified as **8**: mp > 300 °; ^{1}H NMR ($CDCl_3$) δ 10.45 (s, 2 H), 8.48 (d, 2 H, $J = 4.3$ Hz), 8.43 (d, 2 H, $J = 4.3$ Hz), 8.35 (br s, 2 H), 8.22 (m, 4 H), 8.17 (m, 2 H), 8.10 (m, 2 H), 7.9−7.6 (m, 12 H); high res Q-TOF MS, *m*/*z* 808.0604 (calcd for $C_{44}H_{28}79BrN_3O^{130}Te + H$ 808.0607).

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Supporting Information Available: Figure S1 showing the ratio of products **6** and **7** as a function of time under second-order conditions and Figure S2 showing the ratio of products **6** and **7** as a function of time under pseudo-first-order conditions. This information is available free of charge via the Internet at http://pubs.acs.org.

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