Positive Halogens from Halides and Hydrogen Peroxide with Organotellurium Catalysts

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Abstract: The oxidations of sodium bromide, sodium chloride, and sodium iodide to positive halogen with hydrogen peroxide in two-phase systems of dichloromethane and pH 6 phosphate buffer were catalyzed by organotellurium catalysts **1**−**3**. The positive halogens were trapped by cyclohexene for bromine and chlorine to give mixtures of the 1,2-dihalocyclohexane (**4**) and 2-halocyclohexanol (**5**). For the bromination (**4a**)/hydrobromination (**5a**) of cyclohexene, unoptimized turnover numbers of 1010 mol of product per mole of catalyst for **1**, 960 for **2**, and 820 for **3** were measured with **4a**/**5a** ratios of 55:45, 53:47, and 52:48, respectively. In cyclohexane, the turnover number for **1** was 150 and the **4a**/**5a** ratio was 68:32. In the uncatalyzed process and in the reaction of aqueous bromine with cyclohexene, the **4a**/**5a** ratio is 55:45 in dichloromethane and 67:33 in cyclohexane. The relative rates of catalysis for equimolar amounts of **1**−**3** were nearly identical to the relative second-order rate constants for oxidation of the organotellurium compounds with hydrogen peroxide, which suggests that oxidation of the catalyst is the rate-determining step of the process. Stopped-flow studies indicated a rapid reaction ($k = 22.5 \pm 0.3$ M^{-1} s^{-1} for iodide and 13.9 ± 0.5 M^{-1} s^{-1} for bromide) between halide and oxidized **3** to regenerate catalyst **3**. Relative rates of catalysis with 0.1 mol % of **1**−**3** (relative to cyclohexene) were 4.6 for **1**, 2.0 for **2**, 1.0 for **3**, and 0.11 for the control reaction with no catalyst at 296.1 ± 0.1 K. Oxidation of chloride with hydrogen peroxide with **1** as a catalyst was much slower but the unoptimized turnover number was 100 with a **4b**/**5b** ratio of 7:93 (10:90 in the uncatalyzed process) in a two-phase cylohexane/aqueous system. Oxidized **3** reacts rapidly with both sodium chloride and sodium bromide to give products from oxidative addition of halogen to the catalyst. Stronger Te−Cl bonds relative to Te-Br bonds slow down the release of the Te(II) state of the catalyst. Positive iodine from catalysis with **1** was trapped by 4-pentenoic acid to give iodomethyl lactone **6**.

Hydrogen peroxide is both a powerful oxidant from a thermodynamic perspective and an environmentally friendly oxidant yielding oxygen and water upon decomposition. Many reactions of H_2O_2, which are favored thermodynamically, are limited by the kinetics of reaction. Two such reactions are the oxidations of bromide to bromine/hypobromous acid and chloride to chlorine/hypochlorous acid with H_2O_2, which are slow at ambient temperature and neutral pH.[1] In nature, halide oxidations with peroxide are conducted by the haloperoxidase enzymes.[2] Chloroperoxidase[3] and bromoperoxidase[2] enzymes and model systems that mimic their activity[4,5] use a transition metal (heme-bound iron for chloroperoxidase, non-heme vanadium for bromoperoxidase)[2c] to activate H_2O_2 for the oxidation of halide to halogen or hypohalous acid. Model studies have shown that chloride,[6] bromide,[2,5] and iodide[7] can be oxidized by such catalysis and that the metal undergoes sequential one-electron steps. These biomimetic reactions are important to chemistry in general in that they perform many desired chemical transformations such as epoxidations and halogenations in an environmentally acceptable way. However, adaption of enzymatic processes to commercial application is limited by the availability and the chemical and physical constraints of the enzyme.

We report here preparative and mechanistic studies on new main-group organometallic catalysts for the oxidation of halides with hydrogen peroxide in which two-electron redox processes at tellurium mimic the haloperoxidase enzymes but avoid one-electron pathways. Organotellurium compounds **1**−**3**[8−10] (Chart 1) were found to catalyze the formation of positive halogens as

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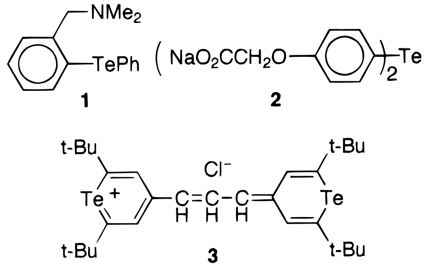
Table 1. Product Ratios and Turnover Numbers for the Oxidation of Sodium Chloride and Sodium Bromide by Hydrogen Peroxide with Organotellurium Catalysts **1**−**3**

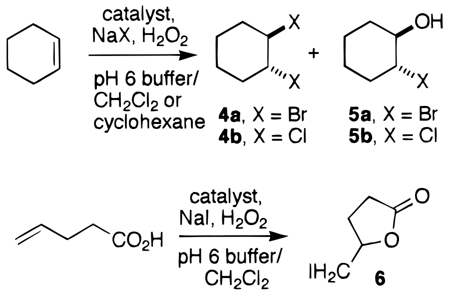
catalyst	$k(H_2O_2)$,[a] L mol^{-1} s^{-1}	halide salt	solvent	k_{rel}(cat)[b]	**4**/**5** ratio	mol of (**4**/**5**)/ mol of catalyst
none		NaBr	CH_2Cl_2	0.11	56:44 (**4a**/**5a**)	
		NaBr	cyclohexane	0.02	67:33 (**4a**/**5a**)	
		NaCl	cyclohexane		10:90 (**4b**/**5b**)	
1	17.1 ± 0.3	NaBr	CH_2Cl_2	4.6	55:45 (**4a**/**5a**)	1010
		NaBr	cyclohexane	0.6	68:32 (**4a**/**5a**)	150
		NaCl	cyclohexane		7:93 (**4b**/**5b**)	100[c]
2	8.94 ± 0.05	NaBr	CH_2Cl_2	2.0	53:47 (**4a**/**5a**)	960
3	2.74 ± 0.03	NaBr	CH_2Cl_2	1.0	52:48 (**4a**/**5a**)	820

[a] Second-order rate constant for oxidation of diorgano telluride at 298.0 ± 0.1 K with H_2O_2. [b] Relative rates of product formation at 296.1 K with no catalyst (controls) or with 0.1 mol % catalyst **1**−**3** (relative to cyclohexene). [c] At reflux.

Chart 1



Scheme 1



exhibited in the bromination/bromohydration and chlorination/chlorohydration of cyclohexene and the iodolactonization of 4-pentenoic acid with H_2O_2 and the corresponding halide salt (Scheme 1). These catalysts were chosen for their solubility in both water and organic solvents for evaluation of two-phase reaction systems. In addition, compound **3** displays huge spectral changes between the Te(II) state [$\lambda_{max}(H_2O)$ 810 nm (ϵ = 150 000)] and the H_2O_2-oxidized states [$\lambda_{max}(H_2O)$ 510 nm (ϵ = 50 000)],[10] which allows facile monitoring of the kinetics of changes in the oxidation state at the catalyst.

Results and Discussion

Preparative Studies. The oxidation of bromide with hydrogen peroxide was followed by the initial rate of formation of **4a** and **5a** in a two-phase system of 0.5 M cyclohexene in CH_2Cl_2 for the organic phase and an aqueous phase of H_2O_2 (3.0 M) and NaBr (2.0 M) in pH 6.0 phosphate buffer at 296.6 ± 0.1 K. The control experiments were then compared to catalyzed reactions at 296.6 ± 0.1 K in which 0.010 mmol of **1**−**3** were added (0.1 mol % relative to cyclohexene, 0.01 mol % relative to H_2O_2) as shown in Figure 1. The stirring rate was held constant for all runs. The **4a**/**5a** ratios were nearly identical in both catalyzed and uncatalyzed reactions (Table 1) and to the 55:45 **4a**/**5a** ratio produced by the addition of cyclohexene to bromine in the aqueous pH 6 buffer. *These data suggest that the same oxidizing species are formed in both the catalyzed and uncatalyzed reactions with NaBr/H_2O_2 and with aqueous bromine.*

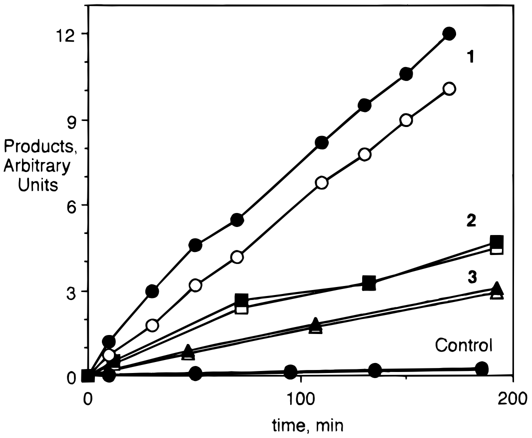


Figure 1. Initial rates of formation of **4a** (filled symbols) and **5a** (open symbols) (as measured by GC) for the oxidation of bromide with hydrogen peroxide catalyzed by 0.010 mmol (0.1 mol % relative to cyclohexene, 0.01 mol % relative to H_2O_2) **1**−**3** in a two-phase system of 0.5 M cyclohexene in CH_2Cl_2 (20 mL) and H_2O_2 (3.0 M) and NaBr (2.0 M) in pH 6.0 phosphate buffer (32.5 mL aqueous volume) at 296.6 ± 0.1 K with stirring at a constant rate. The rates of product formation for catalyzed (**1**−**3**) and uncatalyzed (control) reactions are in arbitrary units and were measured by GC response relative to an internal standard of 1.0 mg/mL of diphenyl ether.

The second-order rate constants for the oxidation of **1**−**3** with H_2O_2 at 298.0 ± 0.1 K were determined under pseudo-first-order conditions and are compiled in Table 1. The relative rates of formation of **4a**/**5a** with catalysts **1**−**3** are remarkably mirrored by the rates of oxidation of **1**−**3** with H_2O_2. The *relative* initial rates of catalysis in Figure 1 under the conditions described above are 1.0 for **3**, 2.0 for **2**, and 4.6 for **1** while the *relative* second-order rate constants for H_2O_2 oxidation of the catalysts to the corresponding telluroxides (Table 1) are 1.0 for **3**, 3.3 for **2**, and 6.2 for **1**. *These relative rates are consistent with the rate-determing step of the catalytic process being the oxidation of the telluride.*

The turnover numbers for these catalysts were obtained from preparative runs with a large excess of cyclohexene and H_2O_2 relative to catalyst. A two-phase system of 50 mL of 0.5 M cyclohexene in CH_2Cl_2, 50 mL of 2.0 M NaBr in pH 6 phosphate buffer, and 12.5 mL of 50% H_2O_2 (3.0 M H_2O_2 overall) with 0.010 mmol of catalyst was stirred at ambient temperature. When the reaction began to slow (as monitored by GC), a second 12.5-mL aliquot of H_2O_2 was added. When reaction began to slow again, the product mixtures were isolated, yields corrected for the uncatalyzed process, and **4a**/**5a** ratios and turnover numbers calculated (Table 1). *The unoptimized turnover numbers listed in Table 1 are in the range 820*−*1010 mol of product/mol of catalyst.*

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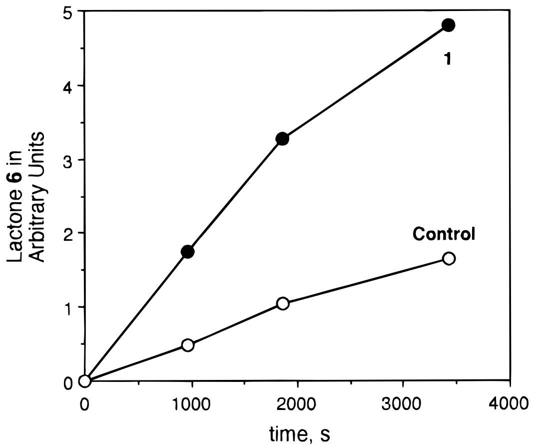


Figure 2. Iodolactonization of 4-pentenoic acid (10 mmol) to give **6** (as measured by GC) with NaI (65 mmol) and H_2O_2 (100 mmol) in a two-phase system of 20 mL of CH_2Cl_2 and 32.5 mL of pH 6 phosphate buffer catalyzed by 0.010 mmol (0.1 mol % relative to cyclohexene, 0.01 mol % relative to H_2O_2) of **1**. The rates of product formation for catalyzed (**1**) and uncatalyzed (Control) reactions are in arbitrary units and were measured by GC response relative to an internal standard of 1.0 mg/mL of diphenyl ether.

Cyclohexane as an environmentally more acceptable solvent than CH_2Cl_2 can be utilized in the two-phase procedure described above. Reaction is somewhat slower at ambient temperature, but the turnover number for **1** after two aliquots of H_2O_2 is 150 mol of product/mol of catalyst and the product ratios again are nearly identical in the catalyzed and uncatalyzed reactions (Table 1).

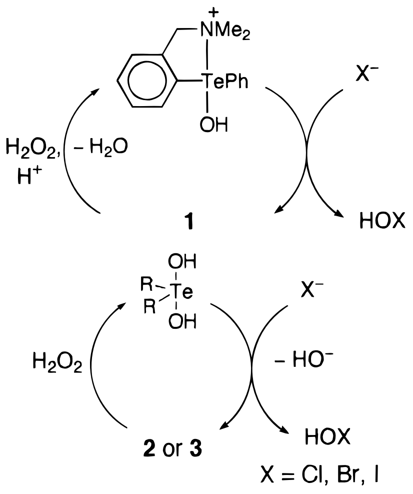
Chloride is also oxidized by H_2O_2 with diorganotelluride catalysis but the process is slower. A two-phase mixture of 0.03 mmol of **1** and 10 mmol of cyclohexene in 20 mL of cyclohexane, 20 mL of 2.0 M NCl in pH 6 phosphate buffer, and 12.5 mL of 50% H_2O_2 (5.5 M H_2O_2 overall) was heated at reflux for 2 h. A second 12.5-mL aliquot of H_2O_2 was added and the reaction mixture was stirred an additional 3 h at reflux. The product mixture was isolated, yield corrected for the negligible uncatalyzed process, and the **4b**/**5b** ratio and unoptimized turnover number of 100 calculated (Table 1).

The oxidation of NaI with H_2O_2 to give HOI/I_2 is also catalyzed by the addition of a diorganotelluride catalyst. The rate of iodolactonization of 4-pentenoic acid (10 mmol) to give **6** (Scheme 1) with NaI (65 mmol) and H_2O_2 (100 mmol) in a two-phase system of 20 mL of CH_2Cl_2 and 32.5 mL of pH 6 phosphate buffer (Scheme 1) was more than doubled by the addition of 0.01 mmol of catalyst **1** (0.1 mol % relative to 4-pentenoic acid, 0.01 mol % relative to H_2O_2) to the reaction mixture (Figure 2). The ease of oxidation of iodide by H_2O_2 renders less dramatic the catalytic efficiency of **1** in this process.

The use of sodium fluoride under the conditions described for the oxidation of sodium chloride in the presence of cyclohexene did not lead to appreciable yields of 1,2-difluorocyclohexane or 2-fluorocyclohexanol with 0.1 mol % of catalyst **1** or **3**.

Mechanistic Studies. One possible mechanistic route for the catalytic role of diorganotellurides is shown in Scheme 2. Based on the similarity of relative rates of catalysis with relative rates of oxidation of catalyst by H_2O_2, we assume the initial step is oxidation of the diorgano telluride to the hydroxy (for **1**) or dihydroxy (for **2** and **3**) Te(IV) derivative. Subsequent nucleophilic attack by halide at ligated hydroxide oxygen would give diorganotelluride and hypohalous acid. Alternatively, addition of halide to a telluroxide intermediate might lead to an $R_2Te(OH)X$ intermediate, which then loses hypohalous acid via either reductive elimination of hypohalous acid or nucleophilic attack of halide at a halide ligand to produce halogen while regenerating the diorganotelluride catalyst. Reactions related to these mechanistic possibilities have been proposed for the oxidation of thiols to disulfides with Te(IV) derivatives.[11]

Scheme 2



In the presence of a large excess of H_2O_2, the formation of higher oxidation states of tellurium is possible as is catalysis via peroxo Te(IV) derivatives.[12] In order to eliminate such possibilities, the chemistry of oxidized telluropyrylium dye **3** was examined under conditions where no excess H_2O_2 is present. This was achieved via the self-sensitized, photochemical generation of singlet oxygen with **3**. Dye **3** is oxidized under these conditions to the same product from oxidation of **3** with H_2O_2.[10] Dye **3** [$\lambda_{max}(H_2O)$ 810 nm ($\epsilon = 150\,000$)] and oxidized dye **3** [$\lambda_{max}(H_2O)$ 510 nm ($\epsilon = 50\,000$)] have distinctly different absorption spectra allowing unequivocal observation of changes in oxidation state.

Stopped-Flow Experiments. The reaction of oxidized dye **3** with sodium halide salts was followed by stopped-flow spectroscopy. In reactions with NaI, the reduction of oxidized dye **3** to regenerate catalyst **3** was the first process observed as shown in Figure 3 for the reaction of 2×10^{-5} M oxidized **3** with 0.25 M NaI at 310.0 ± 0.1 K. A kinetic trace of this process at 670 nm is shown in Figure 4 with an observed pseudo-first-order rate constant of $5.26 \pm 0.03\ s^{-1}$ at pH 6.8. A plot of the pseudo-first-order rate constants as a function of iodide concentration (Figure 5) gave a second-order rate constant of $22.5 \pm 0.3\ M^{-1}\ s^{-1}$ for reaction with iodide.

In the bromide reaction at pH 6.8, the addition of bromide gave a new Te(IV) product with only small changes from the absorption spectra of oxidized **3** and a low conversion to reduced catalyst **3**. The rate of appearance of catalyst **3** at 810 nm is shown in the kinetic trace of Figure 6 (0.1 M NaBr, $k_{obs} = 1.09 \pm 0.5\ M^{-1}\ s^{-1}$ at 310.0 ± 0.1 K) with a second-order rate constant of $13.9 \pm 0.5\ M^{-1}\ s^{-1}$ from the concentration studies. The formation of a new Te(IV) product appears to be a consequence of rapid oxidative addition of bromine to the Te(II) state of catalyst **3** regenerated from oxidized **3** as demonstrated in the two-phase experiments described below.

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[11] (a) Engman, L.; Stern, D.; Pelcman, M.; Andersson, C. M. *J. Org. Chem.* **1994**, *59*, 1973−1979. (b) Detty, M. R.; Friedman, A. E.; Oseroff, A. R. *J. Org. Chem.* **1994**, *59*, 8245−8250.

[12] One reviewer raised the concern that species like $R_2Te(OOH)OH$ and/or $R_2Te(OOH)Br$ might form in the presence of a huge excess of H_2O_2. Polarization of the O−O bond in these intermediates could facilitate nucleophilic attack of halide on the hydroperoxide group releasing HOX and a Te(IV) species, which would be the actual catalytic species. While such species would be novel and are quite intriguing, we have no experimental evidence for such peroxo species, but we cannot rigorously exclude their presence.

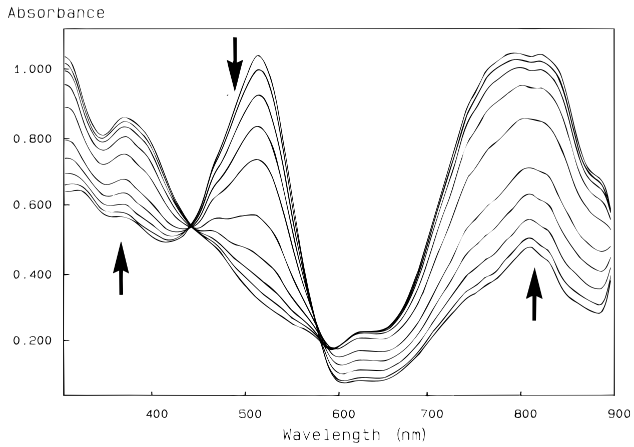


Figure 3. Spectral changes for the reaction of 2 × 10^{-5} M oxidized **3** with 0.5 M NaI at pH 6.8 and 310.0 ± 0.1 K as observed by stopped-flow spectroscopy. Traces from the arrows are at 0.025, 0.062, 0.125, 0.187, 0.25, 0.375, 0.5, 0.625, 0.75, and 1.00 s after mixing.

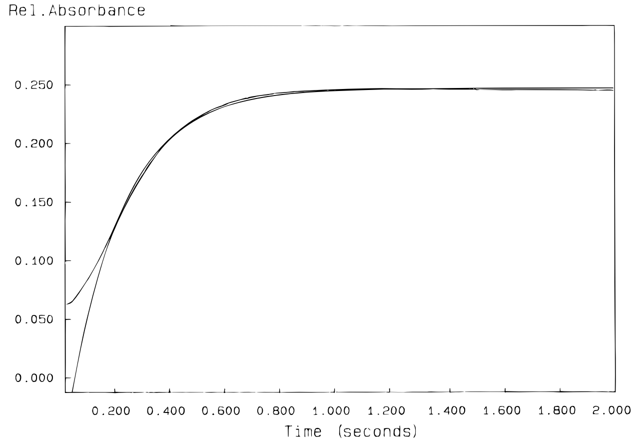


Figure 4. A kinetic trace and first-order curve fitting for the reaction of 2 × 10^{-5} M oxidized **3** with 0.5 M NaI at pH 6.8 and 310.0 ± 0.1 K observed at 670 nm. The observed pseudo-first-order rate constant is 5.26 ± 0.03 s^{-1}.

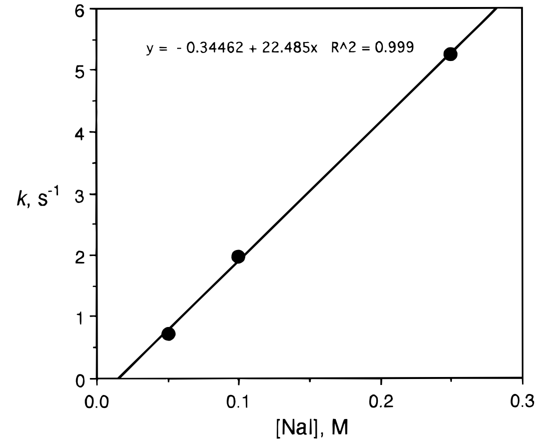


Figure 5. A plot of the pseudo-first-order rate constants measured at iodide concentrations of 0.25, 0.1, and 0.05 M at pH 6.8 vs iodide concentration. The slope of the least-squares fit gave a second-order rate constant of 22.5 ± 0.3 M^{-1} s^{-1} for reaction with iodide.

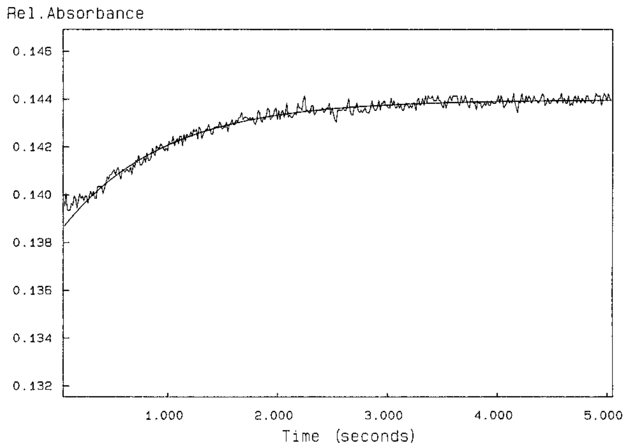
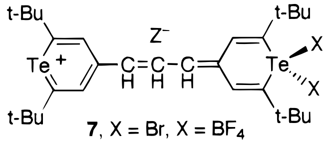


Figure 6. A kinetic trace and first-order curve fitting for the reaction of 2 × 10^{-5} M oxidized **3** with 0.1 M NaBr at pH 6.8 and 310.0 ± 0.1 K observed at 810 nm. The observed pseudo-first-order rate constant is 1.09 ± 0.05 s^{-1}.

Chart 2



7, X = Br, X = BF_4
8, X = Z = Cl

Two-Phase Mechanistic Experiments. A two-phase mixture of a 1.0 × 10^{-5} M CH_2Cl_2 solution of **3** was stirred with an equal volume of pH 6.0 phosphate buffer (50 mL). After equilibration, the absorption spectra of the organic and aqueous phases showed the dye to be mostly in the organic phase (Figure 7a). Irradiation of the mixture gave oxidized **3** (Figure 7b), *which has minimal solubility in the organic phase*. The addition of NaBr to the stirred mixture of Figure 7b gave an immediate loss of color in the aqueous layer and a purple color in the organic phase [Figure 7c, $\lambda_{max}(CH_2Cl_2)$ 563 nm]. The absorption spectrum of the product in the organic phase is identical to that of **7** (Chart 2) in CH_2Cl_2.[13,14] The addition of cyclohexene to the mixture of Figure 7c regenerated the spectra of Figure 3a with stirring. *No other intermediates related to **3** were detected under these conditions.* GC analysis of the concentrated organic phase showed the presence of the 55:45 **4a**/**5a** mixture. In the absence of a substrate such as cyclohexene, product **7** (as the bromide/tribromide salt) would form via the oxidative addition of bromine to **3** from the following equilibrium:

$$\mathrm{HOX} + \mathrm{H^+} + \mathrm{X^-} \rightleftharpoons \mathrm{H_2O} + \mathrm{X_2} \qquad (1)$$

$$\mathrm{X = Cl, Br, I}$$

The absorption spectrum of **7** in water [$\lambda_{max}(H_2O)$ 520 nm (ϵ = 50 000)] is nearly identical to that of oxidized **3**. However, the addition of CH_2Cl_2 to aqueous **7** gives a purple organic phase [$\lambda_{max}(CH_2Cl_2)$ 563 nm (ϵ = 55 000)]. The similarity of the absorption spectra of **7** and oxidized **3** in aqueous solution is not that surprising. However, their solubilities in organic solvents are markedly different.[10,13,14]

Repetition of the photochemical experiment with catalyst **3** with 0.1 M cyclohexene in the organic phase gave formation of the 55:45 **4a**/**5a** mixture. Spectroscopically, catalyst **3** and dibromide **7** were detected in the organic layer while both reduced and oxidized **3** were detected in the aqueous layer in early stages of the reaction. *These data implicate the Te(II)−Te(IV) shuttle in the photochemical catalytic cycle for bromination, not a higher oxidation state tellurium intermediate.* It should also be noted that a control photochemical reaction (no catalyst) gave no detectable formation of either **4a** or **5a**.

No suitable spectral changes for stopped-flow spectroscopy in aqueous solution were observed upon addition of NaCl to

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(13) Detty, M. R.; Luss, H. R. *Organometallics* **1986**, *5*, 2250−2257.
(14) Detty, M. R.; Frade, T. M. *Organometallics* **1993**, *12*, 2496−2504.

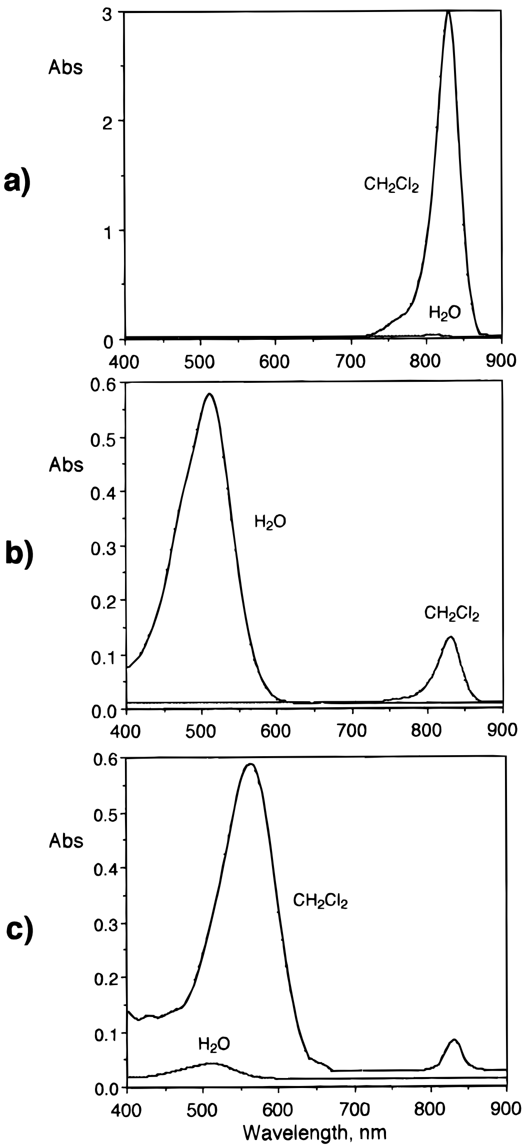


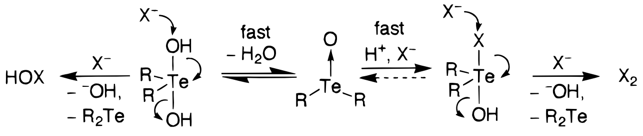
Figure 7. Intermediates formed in the use of catalyst **3** in two-phase systems for the oxidation of sodium bromide with oxidized catalyst **3**. (a) Absorption spectra of aqueous pH 6 phosphate buffer and CH_2Cl_2 following equilibration of 1.0×10^{-5} M **3** in CH_2Cl_2 with the aqueous phase. (b) Distribution of oxidized **3** between aqueous and organic phases following irradiation of the mixture of (a) with a 60-W tungsten bulb. (c) Chromophores in aqueous and organic phases following addition of 0.50 g of NaBr (5 mmol, 0.1 M in the aqueous layer) to the mixture of (b).

oxidized **3**. However, in the two-phase system, the addition of NaCl to oxidized dye **3** gave chlorine oxidative addition product **8** (λ_{max} 548 nm in CH_2Cl_2)[14] in the time frame of mixing. However, the addition of cyclohexene to the mixture containing **8** does not lead to regeneration of the starting catalyst **3** with the formation of **4b** and **5b** in the time frame of the bromide experiments above. Studies of the thermal reductive elimination of halogen from **7** and **8** have shown that the Te−Cl bond is stronger than the Te−Br bond.[14,15] The poorer catalysis observed in the chloride reactions may be due to competitive formation of chlorine oxidative-addition products, which only slowly regenerate the Te(II) state of the catalyst.

Conclusions

Organotellurium compounds **1**−**3** are useful catalysts for the oxidation of aqueous solutions of chloride, bromide, and iodide to the corresponding halogen with H_2O_2. Preparative studies in two-phase systems indicate high turnover numbers for these catalysts. Furthermore, in aerated systems with catalysts such as **3**, the photochemical, self-sensitized generation of singlet oxygen from catalyst may obviate the need for any added oxidant (other than oxygen) for halogenation reactions with this catalyst.

Scheme 3



Mechanistically, the initial step in the reaction is oxidation of the organotellurium compounds to the corresponding telluroxide or dihydroxy Te(IV) derivatives as shown in Scheme 2. Subsequent nucleophilic attack by halide at ligated hydroxide oxygen would give diorganotelluride and hypohalous acid. Alternatively, addition of halide to a telluroxide intermediate might lead to an $R_2Te(OH)X$ intermediate, which then undergoes reductive elimination of HOX or loses halogen via nucleophilic attack of halide at a halide ligand, regenerating the diorganotelluride. These fates for the oxidized species are illustrated in Scheme 3.

It should also be noted that no other intermediates were detected in the time course of the mechanistic and preparative studies. No oxirane intermediates were detected, which minimizes the possibility of epoxidation followed by nucleophilic opening with halide. The chemistry observed at high H_2O_2 concentrations and the chemistry observed under conditions of no excess H_2O_2 are identical, which argues against the involvement of species like $R_2Te(OOH)OH$ and/or $R_2Te(OOH)Br$.[12]

The stopped-flow experiments indicate that the initial reaction *detected* upon mixing involves reduction of Te(IV) to Te(II) consistent with nucleophilic attack of halide at a hydroxide ligand. However, if hydration−dehydration of the telluroxide intermediate and subsequent halide additions were sufficiently fast ($k_{obs} \geq 100\ s^{-1}$) and if the absorption spectra of all Te(IV) intermediates were similar in H_2O, then these processes would be transparent to detection prior to a change in oxidation state.[16]

Experimental Section

General Methods. Solvents (cyclohexane, dichloromethane), cyclohexene, 4-pentenoic acid, sodium chloride, sodium bromide, sodium iodide, and hydrogen peroxide (30% and 50% solutions) were used as received from Aldrich Chemical Co. Two-phase reaction mixtures were mechanically stirred at a constant rate for kinetic runs. Preparative reactions were stirred magnetically. Concentration *in vacuo* was performed on a Büchi rotary evaporator. Nuclear magnetic resonance spectra were recorded on a Varian Gemini-300 instrument with residual solvent signal as internal standard: $CDCl_3$ (δ 7.26). UV−visible−near IR spectra were recorded on a Perkin-Elmer Lambda 12 spectrophotometer equipped with a circulating constant-temperature bath for the sample holder. Gas chromatography was performed on a Shimadzu GC-14A instrument with a 15 m × 0.53 mm ID Rtx-5 column (Crossbonded 95% dimethyl−5% diphenyl polysiloxane) from Restek Corp., 110 Benner Circle, Bellefonte, PA.

Catalyst **1** was prepared according to ref 8. Catalyst **2** was prepared according to ref 9. Hydrolysis of the bis methyl ester with NaOH in aqueous MeOH gave **2** as a white crystalline solid that precipitated from the reaction mixture. Catalyst **3** was prepared according to ref 10. *trans*-1,2-Dihalocyclohexanes **4a** [*m/z* 244 ($C_6H_{10}{}^{81}Br_2$)] and **4b** [*m/z* 152 ($C_6H_{10}{}^{35}Cl_2$)] were prepared by bromination and chlorination, respectively, of cyclohexene in CH_2Cl_2. *trans*-2-Halocyclohexanols **5a** [*m/z* 180 ($C_6H_{11}{}^{81}BrO$)] and **5b** [*m/z* 134 ($C_6H_{11}{}^{35}ClO$)] were prepared

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(15) Detty, M. R.; Fleming, J. C. *Adv. Mater.* **1994**, *6*, 48−51.

(16) Glutathione thiol substitution for hydroxide at Te(IV) in ref 11b is sufficiently fast ($k \geq 5 \times 10^6\ M^{-1}\ s^{-1}$) to mask such a reaction in the current studies.

by ring-opening of cyclohexene oxide (Aldrich Chemical Co.) with aqueous HBr and HCl, respectively. The 2-oxo-4-(iodomethyl)-tetrahydrofuran (**6**) was prepared by the addition of iodine to a dichloromethane solution of 4-pentenoic acid containing 1.2 equiv of pyridine: ^{1}H NMR ($CDCl_3$) δ 4.52 (m, 1 H), 3.39 (ABX, 1 H), 3.27 (ABX, 1 H), 2.35−2.7 (m, 3 H), 1.96 (m, 1 H); IR (film, NaCl) 1776 cm^{-1}; *m/z* 226.5 ($C_5H_7O_2I$).

Kinetic Comparisons. (a) Bromide Oxidations. In typical experiments, 0.010 mmol of catalyst **1**−**3** was added to a two-phase system of 0.5 M substrate [0.820 g (0.0100 mol) of cyclohexene] in CH_2Cl_2 (20 mL) for the organic phase and an aqueous phase of H_2O_2 (12.5 mL of a 30% solution) and NaBr (6.63 g, 0.065 mol) in pH 6.0 phosphate buffer (20 mL) at 296.6 ± 0.1 K. The *trans*-1,2-dibromocyclohexane (**4a**) and *trans*-2-bromocyclohexanol (**5a**) produced in this reaction were identified by GC-mass spectroscopy with comparison to authentic samples for retention time. Relative response factors were measured for standard 5.0×10^{-3} M solutions of **4a** and **5a**. Diphenyl ether (1 mg/mL) was added to the starting solution of cyclohexene as an internal standard for the GC measurements. The organic phase was sampled periodically by gas chromatography (GC) and the relative rates of appearance of **4a** and **5a** for each catalyst are illustrated in Figure 1. These relative rates of appearance of **4a** and **5a** are compared to the appearance of **4a** and **5a** in control reactions in which no catalyst is added. The ratio of products **4a**/**5a** for each catalyst is compiled in Table 1.

(b) Iodide Reactions. In typical experiments, 0.010 mmol of catalyst **1**−**3** was added to a two-phase system of 0.5 M substrate [1.00 g (0.0100 mol) of 4-pentenoic acid] in CH_2Cl_2 (20 mL) for the organic phase and an aqueous phase of H_2O_2 (12.5 mL of a 30% solution) and NaI (9.75 g, 0.065 mole) in pH 6.0 phosphate buffer (20 mL) at 296.6 ± 0.1 K. The 2-oxo-4-(iodomethyl)tetrahydrofuran (**6**) produced in this reaction was identified by GC-mass spectroscopy with comparison to an authentic sample of **6** for retention time. Diphenyl ether (1 mg/mL) was added to the starting solution of 4-pentenoic acid as an internal standard for the GC measurements. The organic phase was sampled periodically by gas chromatography (GC) and the relative rates of appearance of **6** in catalyzed and control (no catalyst) reactions are illustrated in Figure 2.

Preparative Reactions. (a) Bromide Reactions in Dichloromethane. In typical experiments, 0.010 mmol of catalyst **1**−**3** was added to a two-phase system of 0.5 M substrate [2.05 g (0.0250 mole) cyclohexene] in CH_2Cl_2 (50 mL) for the organic phase and an aqueous phase of H_2O_2 (12.5 mL of a 50% solution) and NaBr (10.2 g, 0.100 mol) in pH 6.0 phosphate buffer (50 mL) were stirred at ambient temperature. The reactions were sampled periodically by GC. When the rate of appearance of products began to plateau, a second 12.5-mL aliquot of 50% H_2O_2 was added (approximately 2 h). When reaction began to slow again after 2 h, the organic phase was separated, washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. Bulb-to-bulb transfers at 1 Torr to remove traces of volatiles gave 2.15 ± 0.04 g of the bromination product mixture for **1**, 2.03 ± 0.05 g for **2**, and 1.74 ± 0.04 g for **3** after correcting for the uncatalyzed process (0.044 ± 0.005 g of product mixture). The yields cited are the average of duplicate runs. Product ratios as determined by GC are compiled in Table 1. For the control reaction, the second 12.5-mL aliquot of 50% H_2O_2 was added 2 h after addition of the first. Turnover numbers are compiled in Table 1 and are based on 0.010 mmol of catalyst.

(b) Bromide Reactions in Cyclohexane. The procedure described above was repeated with catalyst **1** (0.0034 g, 0.010 mmol) with cyclohexane replacing dichloromethane as solvent. The second aliquot of H_2O_2 was added after 4 h. The products were isolated 4 h following the second addition of H_2O_2. Following workup, 0.34 ± 0.01 g of a 68:32 mixture of **4a**:**5a** was isolated.

(c) Chloride Reactions in Cyclohexane. The procedure described above was repeated with catalyst **1** (0.0102 g, 0.030 mmol) with cyclohexane as solvent and NaCl (5.80 g, 0.100 mol) replacing NaBr. The two-phase mixture was heated at reflux. The second aliquot of H_2O_2 was added after 2 h. The products were isolated 2 h following the second addition of H_2O_2. Following workup, 0.42 ± 0.01 g of a 7:93 mixture of **4b**:**5b** was isolated.

Oxidation of Catalysts with H_2O_2. The oxidations of **1**−**3** (5×10^{-5} M for **1** and **2**; 2×10^{-5} M for **3**) with 5.0×10^{-3}, 2.5×10^{-3}, and 1.0×10^{-3} M H_2O_2 in pH 6.0 phosphate buffer (prepared by serial dilution) were followed spectrophotometrically at 298.0 ± 0.1 K to completion. The pseudo-first-order rate constants were plotted as a function of [H_2O_2] with the slope of the resulting lines giving the second-order rate constants compiled in Table 1 for **1**−**3**, respectively.

Mechanistic Studies. Spectroscopic Studies with Catalyst 3 in Two-Phase Systems. (a) Bromide Oxidation. A 1.0×10^{-5} M CH_2Cl_2 solution of **3** (50 mL) was stirred with an equal volume of pH 6.0 phosphate buffer (50 mL). After equilibration, the absorption spectra of the organic and aqueous phases showed the dye to be mostly in the organic phase [Figure 3a, λ_{max}(CH_2Cl_2) 830 nm, ϵ = 330 000; λ_{max}(H_2O) 810 nm (ϵ = 150 000)].[10] Irradiation of the mixture with a 60-W tungsten bulb held 10 cm from the Pyrex reaction flask gave oxidized **3** [Figure 3b, λ_{max}(H_2O) 510 nm (ϵ = 50 000)].[10] The addition of 0.50 g of NaBr (5 mmol, 0.1 M in the aqueous layer) to the stirred mixture of Figure 3b gave an immediate loss of color in the aqueous layer and a purple color in the organic phase [Figure 3c, λ_{max}(CH_2Cl_2) 563 nm (ϵ = 55 000)]. The addition of 0.41 g (5.0 mmol, 0.1 M in the organic phase) of cyclohexene to the mixture of Figure 3c regenerated the spectra of Figure 3a with stirring.

The reaction was repeated and the organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The field desorption mass spectrum of the purple product mixture gave a weak parent ion cluster with *m/z* 813 ($C_{29}H_{43}{}^{81}Br_2{}^{130}Te_2$) and a strong ($M^+ - Br$) cluster, consistent with the dibromotelluropyryanyl telluropyrylium cation of structure **7**.

(b) Chloride Oxidation. The procedure described above was repeated except that 0.29 g (5 mmol) of NaCl was added in place of NaBr. The product formed in the organic phase displayed λ_{max}(CH_2Cl_2) 548 nm (ϵ = 53 000). Nearly identical chemistry is observed upon the addition of NaCl rather than NaBr to oxidized dye **3**. The chlorine oxidative addition product **8** (λ_{max} 548 nm in CH_2Cl_2)[15] is formed in the time frame of mixing. However, the addition of cyclohexene to the mixture containing **8** does not lead to regeneration of the starting catalyst **3** (with the formation of **4b** and **5b**) in the time frame of the bromide experiments above. The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The field desorption mass spectrum of the purple product mixture gave a parent ion cluster with *m/z* 661 ($C_{29}H_{43}{}^{35}Cl_2{}^{130}Te_2$), consistent with the dichlorotelluropyranyl telluropyrylium cation of structure **8**.

Stopped-Flow Experiments. All stopped-flow experiments were performed on a Sequential DX17 MV Stopped-Flow Spectrometer (Applied Photophysics, Leatherhead, UK). All experiments incorporated the instrument in stopped-flow mode only. The sample handling unit was fitted with two drive syringes that are mounted inside a thermostated-bath compartment, which allowed for constant temperature experimentation at 310.0 ± 0.1 K. The optical-detection cell was set up in the 10-mm path length. First- and second-order curve fitting and rate constants used a Marquardt algorithm[17] based on the routine Curfit.[18] Absorption spectra at indicated time points were calculated through software provided by Applied Photophysics. This consisted of slicing the appropriate time points across a series of kinetic traces (at different wavelengths) and then splining the points of a specific time group.

A solution of 4×10^{-5} M dye **3** in pH 6.8 buffer (pH-adjusted 0.02 M *N,N'*-piperidine bis(2-ethanesulfonate) disodium salt) was irradiated with a 60 W tungsten bulb held 10 cm from the Pyrex reaction flask to give oxidized **3**. The resulting solution served as the stock solution for the stopped-flow experiments. Sodium bromide (0.5, 0.2, and 0.1 M) and sodium iodide (0.5, 0.2, and 0.1 M) solutions at appropriate molarity were prepared in the pH 6.8 buffer system. A halide stock solution and the oxidized **3** stock solution were mixed at equal volumes in the stopped-flow instrument. The pseudo-first-order rate constants were plotted as a function of [halide] with the slope of the resulting lines giving second-order rate constants of 13.9 ± 0.5 for reaction with bromide and 22.5 ± 0.3 for reaction with iodide.

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