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Tellurapyrylium Dyes as Catalysts for Oxidations with Hydrogen Peroxide and as Scavengers of Singlet Oxygen. Dihydroxytelluranes† as Mild Oxidizing Agents

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Dihydroxytelluranes derived from tellurapyrylium dyes via oxidative addition of hydrogen peroxide or via scavenging of singlet oxygen in the presence of water are useful as mild oxidants. These materials undergo two-electron reductions with values of $E°$ near 0.0 V (vs SCE). The dihydroxytellurane **5c** oxidizes leucodye **3a** to **4a** and leucodye **3b** to **4b** with second-order rate constants of $>1 \times 10^3$ M^{-1} $\mathrm{s}^{-}1$ at 298.0 ± 0.1 K based on the pseudo-first-order appearance of reduced tellurapyrylium dye **7c**. These values are much larger than the second-order rate constants for the oxidation of leucodyes **3** to **4** ($<2 \times 10^{-5}$ M^{-1} s^{-1} at 298.0 ± 0.1 K) with hydrogen peroxide. The dihydroxy tellurane **5c** (10^{-5} M) oxidizes thiophenol (10^{-3} M) to phenyl disulfide in minutes in 75% methanol, based on the pseudo-first-order loss of **5c** at 298.0 ± 0.1 K. This rate is much faster than the uncatalyzed oxidation of thiophenol to phenyl disulfide with hydrogen peroxide in 75% methanol-d_4 (half-life of approximately 1 day). The second-order rate constants for the oxidative addition of hydrogen peroxide to tellurapyrylium dyes **7** and **13** range between 0.139 M^{-1} s^{-1} for **13** and 2.26 M^{-1} s^{-1} for **7c** in distilled water. Consequently, tellurapyrylium dye **7c** and other tellurapyrylium dyes serve as catalysts for hydrogen peroxide oxidations of leucodyes **3** and aromatic thiols via the formation of dihydroxytelluranes as intermediates. Values of k_{cat} of up to 2.25×10^4 M^{-2} s^{-1} for the oxidation of **3a** with turnover numbers of greater than 300 were observed. Neutral tellurium(II) compounds to not catalyze these oxidations. Thiapyrylium dye **20** and selenapyrylium dye **21** did not catalyze these reactions. The second-order rate constants for oxidative addition of hydrogen peroxide are 4.62×10^{-4} and 4.68×10^{-4} M^{-1} s^{-1} in water and 6.98×10^{-6} and 1.09×10^{-5} M^{-1} s^{-1} in 90% methanol for **20** and **21**, respectively. The quantum yield for self-sensitized scavenging of singlet oxygen by tellurapyrylium dyes is solvent dependent, varying from 9.5×10^{-5} for **7c** (1.0×10^{-5} M) in 99% methanol, 1.2×10^{-3} in 50% methanol, to 5.5×10^{-3} in water. The largest contributing factor to this variation is the rate of reaction of singlet oxygen with tellurapyrylium dyes in various solvents. For **7c**, k(ox) increases from 9×10^6 M^{-1} s^{-1} in 99% methanol, 1.8×10^8 M^{-1} s^{-1} in 50% methanol, to 8×10^8 M^{-1} s^{-1} in water. The dihydroxytelluranes formed from scavenging of singlet oxygen can be utilized directly for the oxidation of leucodyes **3** with turnover numbers of >50.

Introduction

Two-electron oxidations and reductions of organoselenium compounds have found synthetic utility in a variety of organic transformations. Perhaps the best studied of these reactions are elimination reactions of selenoxides to give olefins and [2,3] sigmatropic rearrangements of allylic selenoxides to give allylic alcohols.[1] Similar reactions of higher oxidation states of organotellurium compounds have been far fewer in number. The in situ formation of tellurones or tellurinic esters has lead to elimination reactions,[2] and the intramolecular oxidation of carbon adjacent to a telluroxide center has been described.[3]

Arenetellurinic anhydrides have been employed as mild oxidants for a variety of organic substrates[4] including thiols, phosphines, and hydroquinones. Similar reactions have been reported with various telluroxides.[5] Oxidations with dihalotellurium(IV) derivatives have given quinones from hydroquinones, disulfides from thiols, and diselenides from selenols.[6] Hydrolysis of these dihalo derivatives gives telluroxides. A catalytic scheme using 1,2-dibromotetrachloroethane as a brominating agent of tellurium(II) has been developed in which telluroxides produced in situ are the working oxidant.[7]

The pertellurane dibromides **1**, which also have Te in the Te(IV) oxidation state but have an odd number of ligands, function as mild oxidants for ethylmercaptan,

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† Tellurane is appropiately used for the saturated six-membered ring. Tellurane is being used in this paper in a broader sense to include both forms.

(1) (a) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22. (b) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. (c) Sharpless, K. B.; Gordon, K. M.; Lauer, R. F.; Patrick, D. W.; Singer, S. P.; Young, M. W. *Chem. Scr.* **1975**, *8A*, 9. (d) Reich, H. J. In *Oxidation in Organic Chemistry*; Trahanovsky, W., Ed.; Academic Press: New York, 1978; Part C, p 1.

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(6) (a) Barton, D. H. R.; Finet, J.-P.; Giannotti, C.; Thomas, M. *Tetrahedron Lett.* **1988**, *29*, 2671–2674. (b) Detty, M. R.; Luss, H. R. *J. Org. Chem.* **1983**, *48*, 5149–5151.

(7) Ley, S. V.; Meerholz, C. A.; Barton, D. H. R. *Tetrahedron* **1981**, *37*, Suppl. No. 1, 213–223.

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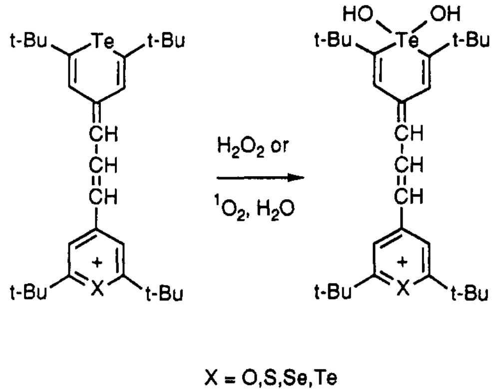
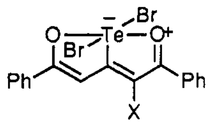
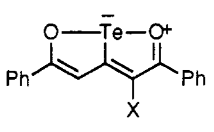
Scheme I



thiophenol, and benzeneselenol.[8] Quantitative yields of ethyl disulfide, phenyl disulfide, and diphenyl diselenide were isolated from the corresponding thiol or selenol as well as the reduced dioxatellurapentalenes **2**.



1a, X = H
b, X = Br



2a, X = H
b, X = Br

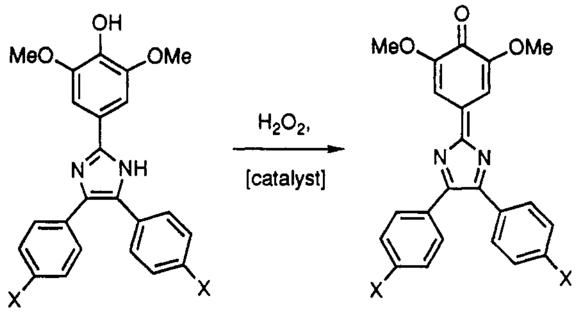
An interesting new class of tellurium(IV) compounds comes from the oxidation of tellurapyrylium dyes with either hydrogen peroxide or with singlet oxygen in the presence of water to give dihydroxytellurane dyes as shown in Scheme I.[3] The dihydroxytelluranes are formally hydrated telluroxides and display a variety of unusual properties which include increased acidity of the protons of the hydroxyl groups and the ability of the tellurium(IV) center in these molecules to oxidize an adjacent carbon center.[3] Like their dihalide analogues, these materials undergo exchange of hydroxy ligands between tellurium(II) and tellurium(IV) as observed by ^{1}H NMR spectroscopy. Of particular interest were the water solubility of the dihydroxytelluranes and the thermal, reductive elimination of hydrogen peroxide from the dihydroxytelluranes to regenerate the tellurapyrylium dye. These properties suggested that tellurapyrylium dyes might be useful as two-electron shuttles for oxidants such as hydrogen peroxide via the dihydroxytellurane as an intermediate. Rate constants for reductive elimination of hydrogen peroxide from the tellurium(IV) center as well as equilibrium constants for tellurapyrylium dye, dihydroxytellurane, and hydrogen peroxide have been measured.[3]

In a preliminary communication, we described catalytic reactions of one tellurapyrylium dye in which a dihydroxytellurium(IV) species was produced as an intermediate.[9] In one reaction, the tellurapyrylium dye is oxidized to the dihydroxytellurane via irradiation of air-saturated aqueous solutions. Thermal reductive elimination of hydrogen peroxide regenerates the starting tellurapyrylium dye, allowing the net photochemical conversion of oxygen and water to hydrogen peroxide. In a second reaction, the formation of the dihydroxytellurane via reaction of a catalytic amount of tellurapyrylium dye with either singlet oxygen and water or with hydrogen peroxide leads to oxidation of leucodyes **3** to dyes **4**. In both of these systems, a tellurium(II)–tellurium(IV)–tellurium(II) cycle avoids the use of a sacrificial electron donor.

Table I. Electrochemical Reduction Potentials of Dihydroxytelluranes 5 and 6 and Dibromotelluranes 9 and 10[a]

compd	$E_{p_c}{}^1$, V (vs SCE)	N, F mol^{-1}	$E_{p_c}{}^2$, V (vs SCE)
5a	−0.18	1.91	−0.48
5b	−0.22	1.84	−0.45
5c	−0.10	2.06	−0.42
6	−0.10		−0.55
9a	−0.05	1.84	−0.48
9b	+0.10		−0.44
9c	+0.24	1.95	−0.45
10	+0.18		−0.55

[a] In 10% aqueous acetonitrile with 0.2 M tetrabutylammonium fluoroborate as supporting electrolyte at a platinum disk electrode at a scan speed of 0.10 V s^{-1}.



3a, X = OMe
3b, X = NMe$_2$

4a, λ_{max} = 515 nm
4b, λ_{max} = 660 nm

The catalytic behavior described above has not been observed with either selena- or thiapyrylium dyes. In this paper, we examine a variety of different chalcogenapyrylium dyes with respect to their ability to catalyze the two-electron oxidation of either leucodyes **3** to **4** or aromatic thiols to disulfides with hydrogen peroxide. The self-sensitized scavenging of singlet oxygen by chalcogenapyrylium compounds was also evaluated in several combinations of methanol and water as well as the coupling of this reaction with other redox chemistry. Tellurapyrylium compounds function as much better catalysts than corresponding thiapyrylium or selenapyrylium compounds for oxidations with hydrogen peroxide and for self-sensitized scavenging of singlet oxygen.

Results and Discussion

Electrochemical Studies. Diorganotellurium(IV) halides display irreversible two-electron reductions by cyclic voltammetry.[8,10] One would expect dihydroxytelluranes **2**, similar in structure to the dihalotelluranes, to show similar behavior. In 10% aqueous acetonitrile (0.2 M tetra-*n*-butylammonium fluoroborate as supporting electrolyte), irreversible reductions were observed for the dihydroxytelluranes **5** and **6** via cyclic voltammetry (5 × 10^{-4} M in **5** or **6**, Pt disk electrode, 0.1 V s^{-1} scan rate). The initial two-electron reduction was followed by a second one-electron reduction (quasireversible or irreversible in aqueous acetonitrile) characteristic of the corresponding tellurapyrylium dye **7** or **8**. Values for the reduction potentials of **5** and **6** are compiled in Table I.

These values can be compared to those of the corresponding dibromotelluranes **9** and **10**, which are also compiled in Table I. In each comparison, the reduction

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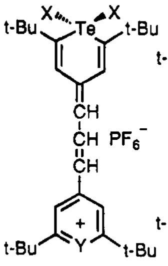
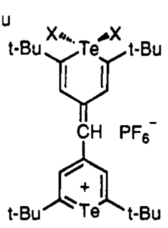
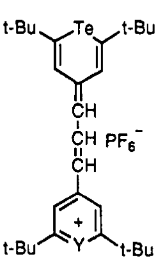


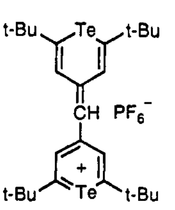
5a, X=OH, Y=S
b, X=OH, Y=Se
c, X=OH, Y=Te
9a, X=Br, Y=S
b, X=Br, Y=Se
c, X=Br, Y=Te



6, X=OH
10, X=Br



7a, Y=S
b, Y=Se
c, Y=Te



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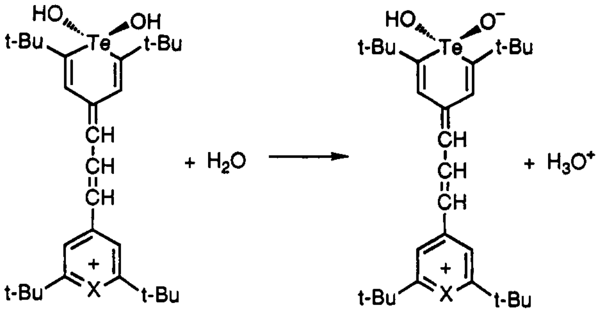
of dihydroxytellurane is 0.13–0.34 V more negative than the corresponding dibromotellurane. In 10% aqueous acetonitrile, the dihydroxytelluranes are presumably dissociated to the zwitterion and a proton ($pK_a = -2$) as illustrated below.[3] The more negative reduction potentials for the dihydroxytelluranes relative to the dibromo telluranes are perhaps related to the differences in net charge between the net positive dibromotelluranes and the net neutral, zwitterionic dihydroxytelluranes.



5 X = S,Se,Te

Bulk electrolyses of solutions of **5** and **9** in aqueous acetonitrile were indicative that the initial irreversible reductions are two-electron processes (Table I). Spectroscopic examinations of the electrolyzed solutions show only the chromophores for the reduced tellurapyrylium dyes **7**. Similarly, cyclic voltammograms of the reduced solutions are indicative of reduced tellurapyrylium dyes **7**.

The reduction potentials listed in Table I suggest that the telluranes should function as mild oxidants. The utility of these dyes as catalysts for the oxidation of leucodyes **3** to dyes **4** with hydrogen peroxide and the utility of these dyes as catalysts for the oxidation of thiols to disulfides with hydrogen peroxide were explored.

Oxidation of Leucodyes 3 and Thiophenol with Dihydroxytellurane 5c. The oxidation of leucodyes **3** to dyes **4** and the oxidation of thiols to disulfides are relatively slow processes with hydrogen peroxide. In aqueous solutions (pH 6.8) containing 1.0×10^{-4} M leucodye **3** and 0.010 M hydrogen peroxide, dyes **4** are formed with pseudo-first-order rate constants of $<1 \times 10^{-8}$ s^{-1} for **3a** and $(1.57 \pm 0.03) \times 10^{-7}$ s^{-1} for **3b** at 298.0 ± 0.1 K. These values correspond to second-order rate constants of $<1 \times 10^{-6}$ M^{-1} s^{-1} for **3a** and $(1.57 \pm 0.03) \times 10^{-5}$ M^{-1} s^{-1} for **3b**.

The oxidation of thiophenol with hydrogen peroxide gives phenyl disulfide. In 75% aqueous methanol-d_4 containing 2.4 M hydrogen peroxide, thiophenol (0.10 M) is oxidized to phenyl disulfide with a pseudo-second-order rate constant of $(7 \pm 2) \times 10^{-4}$ M^{-1} s^{-1} at 296.3 ± 0.1 K, which corresponds to a third-order rate constant of $\sim 3 \times 10^{-4}$ M^{-2} s^{-1}. (The pseudo-second-order rate constants were crudely determined via ^1H NMR spectroscopy and are accurate to the order of magnitude.)

Table II. Solvent-Dependent Values of *k*(ox) and *k*₂ for Tellurapyrylium Dyes 7 and 13, Thiapyrylium Dye 20, and Selenapyrylium Dye 21 at 298.0 ± 0.1 K

compd	solvent	k(ox),[a] M^{-1} s^{-1}	k_2, M^{-1} s^{-1}
7a	water		1.82 ± 0.05
7b	water		1.53 ± 0.03
7c	water	8.0×10^8	2.26 ± 0.02
	50% MeOH	1.8×10^8	0.33[b]
	75% MeOH		0.171 ± 0.002
	90% MeOH		0.080 ± 0.002
	99% MeOH	9.0×10^6	0.013[b]
13	water		0.139 ± 0.005
20	water	9.0×10^6[c]	$(4.62 \pm 0.12) \times 10^{-4}$
	90% MeOH		$(6.98 \pm 0.03) \times 10^{-6}$
21	water	5.0×10^6[c]	$(4.68 \pm 0.06) \times 10^{-4}$
	90% MeOH		$(1.09 \pm 0.01) \times 10^{-4}$

[a] Reference 5b. [b] Reference 3. [c] Value in 50% methanol.

The oxidations of leucodyes **3** and thiophenol with dihydroxytellurane **5c** are much more rapid than oxidations with hydrogen peroxide at 298.0 ± 0.1 K. Both leucodyes **3a** (1.0×10^{-4} M) and **3b** (1.0×10^{-4} M) are oxidized by **5c** (1.0×10^{-5} M) with second-order rate constants of $>1 \times 10^3$ M^{-1} s^{-1} in water (pH 6.8) at 298.0 ± 0.1 K based on the pseudo-first-order appearance of **7c** from **5c**. The oxidation of thiophenol (0.001 M) with **5c** (1.0×10^{-5} M) gives a third-order rate constant of $>5 \times 10^4$ M^{-2} s^{-1} at 298.0 ± 0.1 K in 75% methanol based on the spectroscopic pseudo-first-order loss of **5c** ($>5 \times 10^{-2}$ s^{-1}).

The products of oxidation are the dyes **4** from **3** and phenyl disulfide from thiophenol. Two molecules of water are produced upon reduction of the dihydroxytellurane, as shown in eqs 1 and 2.

$$\mathbf{3} + \mathbf{5c} \rightarrow \mathbf{4} + \mathbf{7c} + 2H_2O \qquad (1)$$

$$2PhSH + \mathbf{5c} \rightarrow PhSSPh + \mathbf{7c} + 2H_2O \qquad (2)$$

The dihydroxytelluranes are kinetically faster oxidants than hydrogen peroxide for the leucodyes **3** and thiophenol. The utility of tellurapyrylium dyes as catalysts for oxidations with hydrogen peroxide will be a function of the rate of oxidative addition of hydrogen peroxide across tellurium. Values for the second-order rate constant, k_2, for the oxidative addition of hydrogen peroxide to dyes **7** and **13** in water and to **7c** in 75% methanol and water are compiled in Table II. As shown in Table II, the second-order rate constants for these dyes vary between 0.139 M^{-1} s^{-1} in water for **13** and 2.26 M^{-1} s^{-1} in water for **7c**, implying that dihydroxytelluranes should form at a kinetically useful rate via the oxidative addition of hydrogen peroxide across the tellurium atom of tellurapyrylium dyes.

Oxidation of Leucodyes 3 with Hydrogen Peroxide Using Tellurapyrylium Catalysts. Tellurapyrylium dyes catalyze the oxidation of leucodyes **3** to dyes **4** with hydrogen peroxide in aqueous solutions (pH 6.8). Values of the pseudo-first-order rate constants, k_{app}, for oxidation of leucodyes **3** (1.0×10^{-4} M) with hydrogen peroxide (0.01 M) as well as catalysis rate constants, k_{cat}, are compiled in Table III. The k_{cat} values were derived from

$$-d[\mathbf{3}]/dt = \{k_{cat}[cat]\}[\mathbf{3}][H_2O_2] \qquad (3)$$

where the product of k_{cat} and catalyst concentration are the effective second-order rate constant for the oxidation described in eq 1. ($k_{H_2O_2}[\mathbf{3}][H_2O_2]$ is small and is omitted.) Dividing by [**3**] gives

$$-d[\mathbf{3}]/[\mathbf{3}]\ dt = k_{app} = \{k_{cat}[cat]\}[H_2O_2] \qquad (4)$$

where $-d[\mathbf{3}]/[\mathbf{3}]\ dt$ is identical to k_{app}, the pseudo-first-

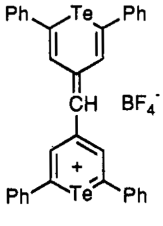
Table III. Pseudo-First-Order Rate Constants (k_{app}) and Conversion Rates (k_{cat}) for Chalcogenapyrylium Dyes And Neutral Tellurium(II) Species as Catalysts for the Oxidation of Leucodyes 3 in Water (pH 6.8) with 0.01 M Hydrogen Peroxide at 298.0 ± 0.1 K

catalyst	conc, M	subst	k_{app}, s^{-1}	k_{cat}, M^{-2} s^{-1}
7a	1.0×10^{-5}	**3a**	$(9.11 \pm 0.02) \times 10^{-4}$	9.11×10^{3}
	1.0×10^{-5}	**3b**	$(1.62 \pm 0.03) \times 10^{-3}$	1.62×10^{4}
7b	1.0×10^{-5}	**3a**	$(1.19 \pm 0.05) \times 10^{-3}$	1.19×10^{4}
	1.0×10^{-5}	**3b**	$(1.33 \pm 0.04) \times 10^{-3}$	1.33×10^{4}
7c	1.0×10^{-5}	**3a**	$(2.25 \pm 0.03) \times 10^{-3}$	2.25×10^{4}
	1.0×10^{-5}	**3b**	$(1.98 \pm 0.05) \times 10^{-3}$	1.98×10^{4}
	1.0×10^{-6}	**3a**	$(1.86 \pm 0.04) \times 10^{-4}$	1.86×10^{4}
8	1.0×10^{-5}	**3a**	$(1.65 \pm 0.09) \times 10^{-4}$	1.65×10^{3}
11	1.0×10^{-5}	**3a**	$(1.18 \pm 0.06) \times 10^{-4}$	1.18×10^{3}
	1.0×10^{-5}	**3b**	$(2.05 \pm 0.08) \times 10^{-5}$	2.03×10^{2}
12	3.0×10^{-5}	**3a**	$(4.25 \pm 0.02) \times 10^{-5}$	1.42×10^{2}
	1.0×10^{-5}	**3b**	$(3.82 \pm 0.06) \times 10^{-5}$	3.80×10^{2}
13	1.0×10^{-6}	**3a**	$(1.24 \pm 0.02) \times 10^{-5}$	1.24×10^{3}
	1.0×10^{-6}	**3b**	$(1.02 \pm 0.01) \times 10^{-5}$	1.01×10^{3}
14	1.0×10^{-5}	**3a**	$(5.52 \pm 0.08) \times 10^{-6}$	5.52×10^{1}
15	2.0×10^{-5}	**3a**	$(1.08 \pm 0.01) \times 10^{-6}$	5.40
	2.0×10^{-5}	**3b**	$(1.82 \pm 0.03) \times 10^{-6}$	8.33
16	2.0×10^{-5}	**3a**	$(8.10 \pm 0.10) \times 10^{-8}$	4.05×10^{-1}
17	1.0×10^{-4}	**3b**	$(1.71 \pm 0.03) \times 10^{-6}$	1.55
18	1.0×10^{-5}	**3b**	$(8.70 \pm 0.15) \times 10^{-8}$	8.7×10^{-1}
19	1.0×10^{-5}	**3a**	$<1 \times 10^{-8}$	$<10^{-1}$
20	1.0×10^{-5}	**3a**	$(8.12 \pm 0.13) \times 10^{-8}$	8.12×10^{-1}
21	1.0×10^{-4}	**3a**	$(7.57 \pm 0.06) \times 10^{-7}$	7.57×10^{-1}
	1.0×10^{-5}	**3b**	$(2.75 \pm 0.15) \times 10^{-8}$	2.75×10^{-1}

order rate constant observed for the disappearance of **3** or the appearance of **4**. Thus, one can solve for k_{cat} where

$$k_{cat} = k_{app}/[\mathrm{cat}][\mathrm{H_2O_2}] \tag{5}$$

A variety of tellurapyrylium dye structures catalyze the oxidation. The most efficient are dyes **7** ($k_{cat} \approx 10^4$) followed by the monomethine analogues **8** and **11** and the dimethylanilino analogue **13** ($k_{cat} \approx 10^3$). The benzoanalogue **12** and the dimethylanilino dye **14** are 1–2 orders of magnitude less efficient still ($k_{cat} \approx 10^2$). The simple tellurapyrylium salts **15** and **16** show little if any catalytic activity ($k_{cat} \approx 10^0$–10^{-1}).



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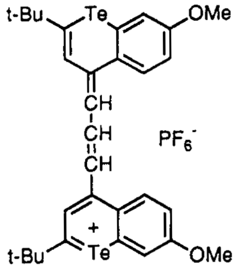

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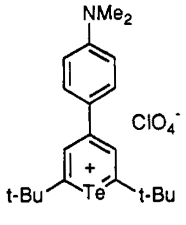

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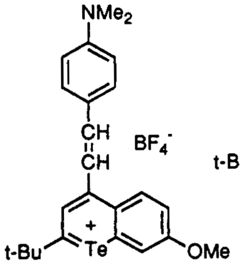

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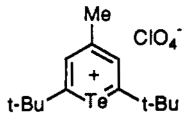

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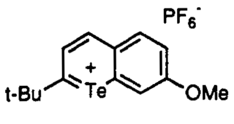

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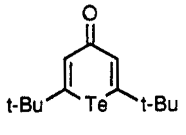
When the rate constant for reaction of **3** and dihydroxytellurane is much larger than the rate constant for reaction of hydrogen peroxide and tellurapyrylium dye, the upper limit of k_{cat} will be determined by the rate of reaction of peroxide with catalyst in these systems to produce dihydroxytellurane. In fact, the product of k_{app} and [3] (from Table III) is nearly identical to the product of k_2 (for the oxidative addition of peroxide to dye, Table II), [cat], and [H_2O_2].

The other indicator of catalyst effectiveness is the turnover number. Turnover numbers are high with tellurapyrylium dyes as illustrated for **7c** and **13**. At 3.0×10^{-7} M in tellurapyrylium dye, complete conversion of **3a** to **4a** (1.0×10^{-4} M) was realized with both **7c** and **13**, corresponding to turnover numbers of >330.

The neutral tellurium(II) compounds **17–19** display little, if any, catalytic activity for the oxidation of leucodyes **3** with hydrogen peroxide (Table III). Tellurapyranone **17**, β-aryltellurocinnamic acid **18**, and diaryl telluride **19** all gave values of k_{cat} for the conversion of **3a** to **4a** of less than 2.0 M^{-1} s^{-1}.



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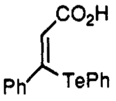

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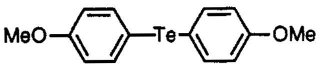

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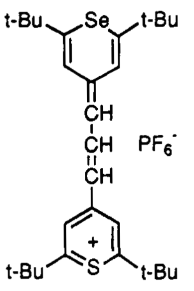

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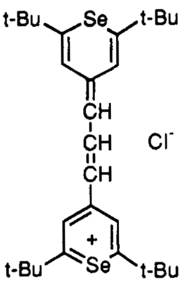

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Thiapyrylium and Selenapyrylium Dyes. Selenapyrylium and thiapyrylium dyes **20** and **21** are much slower catalysts for the oxidation of **3a** to **4a** with hydrogen peroxide than their tellurium analogues **7** (Table III). With identical hydrocarbon frameworks, the values of k_{cat} for **20** (8.12×10^{-1} M^{-1} s^{-1}) and for **21** (7.57×10^{-1} M^{-1} s^{-1}) are more than 4 orders of magnitude smaller than those of the tellurapyrylium dyes **7**.

The oxidative addition of of hydrogen peroxide to **20** and **21** would produce dihydroxysulfurane and dihydroxyselenane species, respectively. Reduction potentials for both of these classes should be similar to the values obtained for the dihydroxytelluranes **7**. Catalytic enhancements of the rate of oxidation of leucodyes **3** to **4** with hydrogen peroxide were much smaller with **20** (k_{cat} = 8.12 M^{-1} s^{-1}) and **21** (k_{cat} = 7.57×10^{-1} M^{-1} s^{-1}) than with **7c** ($k_{cat} \approx 2 \times 10^4$ M^{-1} s^{-1}). Either reduction potentials for the oxidized thia- and selenapyrylium species are much more negative than for the dihydroxytelluranes (which seems unlikely) or the dihydroxysulfurane and dihydroxyselenane intermediates are not formed at a kinetically significant rate.

Second-order rate constants for the disappearance of either **20** or **21** (k_2) in the presence of hydrogen peroxide (0.01–1.0 M) were measured both in water and in 90% methanol under pseudo-first-order conditions (1×10^{-5} M dye, 1.0 M hydrogen peroxide) and are compiled in Table II. In water, k_2 for **20** was measured to be $(4.62 \pm 0.12) \times 10^{-4}$ M^{-1} s^{-1} and k_2 for **21** was measured to be $(4.68 \pm 0.06) \times 10^{-4}$ M^{-1} s^{-1} at 298.0 ± 0.1 K. In 90% methanol, k_2 for **20** was measured to be $(6.98 \pm 0.03) \times 10^{-6}$ M^{-1} s^{-1} and k_2 for **21** was measured to be $(1.09 \pm 0.01) \times 10^{-5}$ M^{-1}

Table IV. Electrochemical Reduction Potentials of Dihalotelluranes 9c, 10, and 22–26[a]

compd	$E_{pc}{}^1$, V (vs SCE)	N, F mol^{-1}	$E^{\circ 2}$, V (vs SCE)
22	−1.14		−1.60
23	−0.68		−1.60
24	−0.46	2.10	−1.60
25	+0.48	1.90	−0.45
26	+0.28		−0.42
9c	+0.17		−0.30
10	+0.35		−0.42

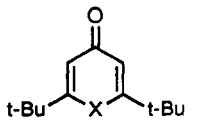
[a] In dichloromethane with 0.2 M tetrabutylammonium fluoroborate as supporting electrolyte at a platinum disk electrode at a scan speed of 0.10 V s^{-1}.

s^{-1} at 298.0 ± 0.1 K. These values are roughly 4 orders of magnitude smaller than those of dyes **7** in identical solvents (2.26 M^{-1} s^{-1} in water and 0.080 M^{-1} s^{-1} in 90% methanol for **7c**) and are consistent with the roughly 4 orders of magnitude smaller values of k_{cat} for **20** and **21** relative to dyes **7**. Furthermore, the product of k_{app} and [**3**] (from Table III) is much less than the product of k_2, [cat], and [H_2O_2], suggesting that products other than dihydroxysulfuranes and dihydroxyselenanes may be formed upon reaction of **20** or **21** with hydrogen peroxide.

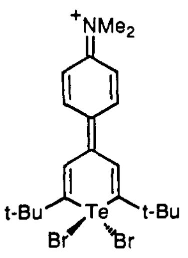
Simple Tellurapyrylium Salts and Neutral Tellurium(II) Species. The data in Table III indicate that the tellurapyrylium dyes are more efficient as catalysts for the oxidation of leucodyes **3** with hydrogen peroxide than are simple tellurapyrylium salts (**15** and **16**) or neutral organotellurium(II) compounds (**17–19**). Oxidative addition of hydrogen peroxide to either **15** or **16** would destroy the aromaticity of the tellurapyrylium ring as well as destabilize the positive charge. Tellurapyrylium dyes **7**, **8**, and **11–14** contain a second aromatic nucleus which maintains delocalization and stabilization of the positive charge. Thus, one might expect the rate of oxidative addition of hydrogen peroxide for the dyes **7**, **8**, and **11–14** to be much greater than for simple tellurapyrylium salts such as **15** or **16**.

Reduction of the dihydroxytellurane formed from the tellurapyrylium dye would regenerate the tellurapyrylium nucleus. The reduction potentials of the dihydroxytelluranes **5** and **6** are positive relative to reduction potentials observed for neutral tellurium(IV) species. Although we were unsuccessful in our attempts to measure reduction potentials for the dihydroxytellurane analogues of **17–19**, comparison to dihalo and bis(acetate) analogues illustrates the effect of the positive charge on reduction potential.

The telluranes **22–24** have been prepared by the oxidative addition of peracetic acid, chlorine, and bromine, respectively, to tellurapyranone **17**.[7] Similarly, **25** was prepared by the oxidative addition of bromine to **13**,[7] while **26** was prepared by the oxidative addition of chlorine to **8**. Reduction potentials for **9c**, **10**, and **22–26** were determined by cyclic voltammetry in dichloromethane. Data are compiled in Table IV.



17, X=Te
22, X=Te(OAc)$_2$
23, X=TeCl$_2$
24, X=TeBr$_2$



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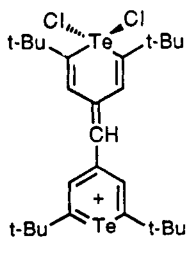

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The positive charge in the dihalotelluranes derived from tellurapyrylium dyes leads to reduction potentials that are 0.6–1.0 V more positive than dihalotelluranes derived from neutral tellurapyranone **17**. If these differences in reduction potential between dihalotelluranes derived from tellurapyrylium dyes **7**, **8**, and **11–14** and dihalotelluranes derived from neutral organotellurium compounds **17–19** were extended to the corresponding dihydroxy analogues, then the dihydroxytelluranes derived from the tellurapyrylium dyes would be more powerful oxidants than the dihydroxytelluranes derived from **17–19**.

Oxidation of Aromatic Thiols to Disulfides with Hydrogen Peroxide Using Tellurapyrylium Catalysts. The oxidation of thiophenol to phenyl disulfide with hydrogen peroxide is a relatively slow process at 296.3 ± 0.1 K with a half-life of approximately 1 day. In 75% methanol-d_4 containing 2.4 M hydrogen peroxide and 0.100 M thiophenol, the addition of 1.0 × 10^{-4} M **7c** gave complete oxidation of thiophenol to phenyl disulfide within 5 min at 296.3 ± 0.1 K.

Similar results were obtained upon the addition of 3.3 × 10^{-4} M **13** to the methanol-d_4 solution of thiophenol and hydrogen peroxide. Complete oxidation was observed within 5 min at 296.3 ± 0.1 K.

The addition of 1.0 × 10^{-3} M **15**, **17**, or **19–21** (1.0 mol %) to the methanol-d_4 solution of thiophenol and hydrogen peroxide gave rates of oxidation essentially identical to those of the uncatalyzed reaction by ^{1}H NMR. Thus, structural requirements for the catalyst appear to be identical in both the oxidation of leucodyes **3** and the oxidation of thiophenol.

On a preparative scale, the addition of 1.5 × 10^{-4} M **7c** to 100.0 mL of a 9.15 × 10^{-2} M solution of thiophenol in 75% methanol containing 2.4 M hydrogen peroxide gave a 97.8% isolated yield of phenyl disulfide after 0.5 h at ambient temperature. This corresponds to a turnover number of ≥320 for **7c** for the production of phenyl disulfide. Similarly, the addition of 1.4 × 10^{-4} M **13** to 100.0 mL of a 9.97 × 10^{-2} M solution of thiophenol in 75% methanol containing 2.4 M hydrogen peroxide gave a 96.9% isolated yield of phenyl disulfide after 0.5 h, corresponding to a turnover number of ≥340 for **13**.

Preparative oxidations of *p*-methoxybenzenethiol and *p*-fluorobenzenethiol with hydrogen peroxide in 75% methanol were also accelerated by the addition of 0.5 mol % **7c**. *p*-Methoxyphenyl disulfide and *p*-fluorophenyl disulfide were isolated in 98.5 and 97.1% yield, respectively, following hydrogen peroxide oxidation of the corresponding thiol after 0.5 h in the presence of the tellurapyrylium catalyst. These yields correspond to turnover numbers of ≥190 for **7c**.

Catalytic Generation of Hydrogen Peroxide from Irradiation of Chalcogenapyrylium Dyes. The photochemical generation of dihydroxytellurane species as oxidants could drive a variety of reactions for light-to-chemical energy conversions. The development of methods for light-to-chemical energy conversion is important for application to solar energy storage. While the major emphasis in such research has been the splitting of water for the production of hydrogen,[11–16] the photoproduction of

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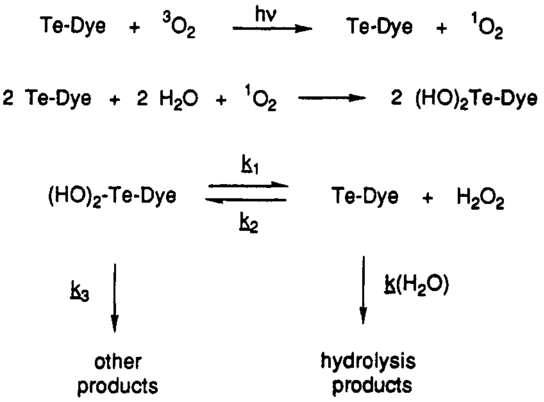
(11) For Ru(2,2′-bipyridine)$_3{}^{2+}$/methylviologen systems: (a) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (b) *Photogeneration of Hydrogen*; Harriman, A., West, M. A., Eds.; Academic: London, 1982. (c) *Energy Resources through Photochemistry and Catalysis*; Gratzel, M., Ed.; Academic: New York, 1983. (d) Prasad, D. R.; Khoffman, M. Z. *J. Am. Chem. Soc.* **1986**, *108*, 2568.

Table V. Parameters for Determining Quantum Efficiencies of Hydrogen Peroxide Generation at 10^{-5} M Catalyst in Water and Aqueous Methanol at 298 K

compd	solvent	$\Phi(^1O_2)^a$	k(ox), M^{-1} s^{-1}	f	turnover number	$\Phi(H_2O_2)$
7a	99% MeOH	0.07		0.92	11.1 ± 2.9	$3.1 \times 10^{-5\,a}$
7b	99% MeOH	0.09		0.84	5.1 ± 0.5	$3.4 \times 10^{-5\,a}$
7c	H_2O	0.12	$8.0 \times 10^{8\,b}$	0.99	89.0 ± 2.6	5.5×10^{-3}
	50% MeOH	0.12	$1.8 \times 10^{8\,b}$	0.97	33.4 ± 2.2	1.2×10^{-3}
	99% MeOH	0.12	$9.0 \times 10^{6\,b}$	0.89	8.7 ± 1.4	9.5×10^{-5}
8	99% MeOH	0.07	9.0×10^{6}	0.60	1.5 ± 0.4	3.8×10^{-5}
11	99% MeOH	0.09	1×10^{7}	0.62	1.7 ± 0.4	5.0×10^{-5}

[a] k(ox) was assumed to be approximately one-half of the value for the Te/Te analogue **7c**. [b] Reference 5b.

Scheme II



other energy-rich compounds such as hydrogen peroxide has also received attention.[11c,17-19] In metal-based systems for the production of either hydrogen or hydrogen peroxide as well as in non-tellurium-containing, dye-mediated systems, a sacrificial electron donor is required to minimize electron back-transfer from the electron relay.

We have reported the photochemical conversion of oxygen and water to hydrogen peroxide using tellurapyrylium dye **7c** as a catalyst.[9] In this process, the photochemical generation of singlet oxygen is followed by the rapid reaction of singlet oxygen and water to produce the dihydroxytellurane **5c**. A slower thermal reaction produces hydrogen peroxide and regenerates the tellurapyrylium catalyst via a reductive elimination reaction. No sacrificial electron donor is required since the tellurapyrylium dye acts as a two-electron shuttle. The catalyst is lost by competitive photochemical or thermal reactions, which include hydrolysis of the dye. This process should be applicable to tellurapyrylium dyes in general, as summarized in Scheme II. Either the hydrogen peroxide generated in this manner or the dihydroxytelluranes produced would use solar energy to store chemical energy.

Stoichiometry of Tellurapyrylium Dye Oxidation with Singlet Oxygen. The stoichiometry for the reaction of singlet oxygen with tellurapyrylium dyes **7** shown in Scheme I was confirmed from studies employing an oxygen electrode. For 6.2×10^{-5} M **7b**, irradiation for 200 s gave complete conversion of **7b** to **5b** and a decrease in oxygen concentration of $(2.2 \pm 0.3) \times 10^{-5}$ M for five independent runs, corresponding to 2.8 ± 0.3 molecules of **7b** oxidized for each molecule of oxygen consumed. For 9.3×10^{-5} M **7c**, irradiation for 100 s gave a decrease in oxygen concentration of $(4.0 \pm 0.3) \times 10^{-5}$ M for five independent runs and complete conversion of **7c** to **5c**, corresponding to 2.3 ± 0.2 molecules of **7c** oxidized for each molecule of oxygen consumed.

The oxygen consumption during oxidation of tellurapyrylium dyes with singlet oxygen roughly corresponds to two molecules of dye oxidized for each oxygen molecule consumed. The concentration of dye employed in these studies is much greater than those employed for studies determining rates of reaction of dyes **7** with singlet oxygen and quantum yields of singlet oxygen generation. Furthermore, complete oxidation of dyes **7** to dihydroxytelluranes **5** in the oxygen electrode studies allows both **5** and **7** to compete for singlet oxygen and introduces some error in the measurement. The oxidized dyes **5** produce singlet oxygen much less efficiently $[\Phi(^1O_2) \leq 0.004]^{8b}$ than the dyes **7** $[\Phi(^1O_2) = 0.07\text{–}0.12]$ such that singlet oxygen produced from irradiation of oxidized dyes **5** should not affect the end point.

Quantum Yield for the Scavenging of Singlet Oxygen from Self-Sensitized Generation. In Scheme II, the photochemical process determines the maximum efficiency of the system while the thermal reactions determine the effective rate of hydrogen peroxide production. The expression for the quantum yield of scavenging of singlet oxygen from self-sensitized generation or the quantum yield for hydrogen peroxide generation is given in eq 6, where $\Phi(H_2O_2)$ is the photochemical quantum yield

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(12) For $Ru(2,2'\text{-bipyridine})_3^{2+}$/bipyridinium systems: Frank, A. J.; Willner, I.; Goren, Z.; Degani, Y. *J. Am. Chem. Soc.* **1987**, *109*, 3568, and references cited therein.

(13) For other a-diimine Ru^{2+} systems: (a) Kalyanasundaram, K. *Coord. Chem. Rev.* **1978**, *7*, 432. (b) Turro, N. J.; Gratzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 675. (c) Fendler, J. H. *J. Phys. Chem.* **1980**, *84*, 1485. (d) Calvin, M. *Photochem. Photobiol.* **1983**, *37*, 349. (e) Dressick, W. J.; Cline, J., III; Demas, J. N.; Degraff, B. A. *J. Am. Chem. Soc.* **1986**, *108*, 7567.

(14) For metalloporphyrin-based systems: (a) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. IIIa, Chapter 1. (b) Kalyanasundaram, K.; Gratzel, M. *Helv. Chim. Acta* **1980**, *63*, 478. (c) Lehn, J. M.; Sauvage, J. P.; Ziessel, R. *Nouv. J. Chim.* **1980**, *4*, 355. (d) Johansen, O.; Mau, A. W.; Sasse, W. H. F. *Chem. Phys. Lett.* **1983**, *94*, 107. (e) Harriman, A.; Porter, G.; Wilowska, A. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 191. (f) Blondell, G.; Dekeukeleire, D.; Harriman, A.; Milgrom, L. R. *Chem. Phys. Lett.* **1985**, 77.

(15) For intramolecular tethering of quencher to sensitizer: (a) Fendler, J. H. *J. Phys. Chem.* **1985**, *89*, 2730. (b) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(16) For colloidal and particulate semiconductor dispersions: (a) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 2239. (b) Duonghong, D.; Borgarello, E.; Gratzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 4685. (c) Fox, M. A.; Lindig, B.; Chen, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 5828. (d) Mau, A. W. H.; Huang, C.-B.; Kakuta, N.; Bard, A. J.; Campion, A.; Fox, M. A.; White, J. M.; Webber, S. E. *J. Am. Chem. Soc.* **1984**, *106*, 6537. (e) Harada, H.; Sakata, T.; Ueda, T. *J. Am. Chem. Soc.* **1985**, *107*, 1773. (f) Kamat, P. V. *Langmuir* **1985**, *1*, 608. (g) Yanagida, S.; Mizumoto, K.; Pac, C. *J. Am. Chem. Soc.* **1986**, *108*, 647. (h) *Homogeneous and Heterogeneous Photocatalysis*; Pelizett, E., Serpone, N., Eds.; Reidel Publishing Co.: Dordrecht, The Netherlands, 1986.

(17) (a) *Photochemical Conversion and Storage of Solar Energy*; Connolly, J. S., Ed.; Academic: New York, 1981. (b) *Photochemical, Photoelectrochemical and Photobiological Processes*; Hall, D. O., Palz, W., Pirrwitz, D., Eds.; Reidel Publishing Co.: Dordrecht, The Netherlands, 1983; Series D, Vol. 2.

(18) Dye-mediated intracellular production of hydrogen peroxide: Martin, J. P.; Logsdon, N. *Arch. Biochem. Biophys.* **1987**, *256*, 39.

(19) $Ru(2,2'\text{-bipyridine})_3^{2+}$ systems for hydrogen peroxide production: (a) Albery, W. J.; Foulds, A. W.; Daruent, J. R. *J. Photochem.* **1982**, *19*, 37. (b) Navarro, J. A.; Roncel, M.; De la Rosa, F. F.; De la Rosa, M. A. *Photochem. Photobiol.* **1987**, *40*, 279. (c) Kurimura, Y.; Nagashima, M.; Takato, K.; Tsuchida, E.; Kaneko, M.; Yamada, A. *J. Phys. Chem.* **1982**, *86*, 2432. (d) Y. Kurimura, Y.; Katsumata, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2560.

(20) Fujihara, H.; Mima, H.; Ikemori, M.; Furukawa, N. *J. Am. Chem. Soc.* **1991**, *113*, 6337–6338.

$$\Phi(H_2O_2) = \Phi(^1O_2)\frac{k(\text{ox})[\text{dye}]}{1/\tau + k(\text{ox})[\text{dye}]}f \qquad (6)$$

for hydrogen peroxide production or scavenging of singlet oxygen from self-sensitized generation, $\Phi(^1O_2)$ is the quantum yield for dye-sensitized generation of singlet oxygen, k(ox) is the rate of reaction of singlet oxygen with the dye, τ is the lifetime of singlet oxygen in the medium, and f is the frequency of singlet oxygen scavenging from the catalyst relative to other reaction pathways in the entire process. Values for these parameters are compiled in Table V for the dyes **7**, **8**, and **11** in 99% methanol at 10^{-5} M and for **7c** in 99% methanol, and 50% methanol, water. Under these conditions, $1/\tau$ is 1×10^5 s^{-1} in 99% methanol, 1.7×10^5 s^{-1} in 50% methanol, and 2.4×10^5 s^{-1} in water.[8b] The assumption was made for monomethine dyes **8** and **11** that the value of k(ox) in methanol was identical to the value for 99% methanol.

Turnover Numbers for Hydrogen Peroxide Generation with Tellurapyrylium Dyes. The utility of tellurapyrylium dyes as catalysts for the production of hydrogen peroxide will be limited by the number of turnovers before consumption of catalyst. These numbers were calculated experimentally for the dyes **7**, **8**, and **11**. Solutions containing 1.0×10^{-5} M tellurapyrylium dye in 99% methanol were irradiated with filtered light from a quartz–halogen source (630–850 nm) until $<10^{-7}$ M dye and dihydroxytellurane dye were detected. At this point, aqueous solutions of leucodye **3a** (10^{-3} M) and the enzyme horseradish peroxidase (HRP) (10^{-12} M) were added. The final concentration of dye **4a** (ϵ 45 000 L mol^{-1}) was measured. The concentration of **4a** was presumed to correspond to the concentration of hydrogen peroxide and dihydroxytellurane produced during irradiation. In 50% methanol and in water, the solutions of **7c** were irradiated until $<10^{-7}$ M **7c** remained. The leucodye **3a** was added, generating **4a** from oxidation with dihydroxytellurane **5c** and from oxidation with hydrogen peroxide (catalyzed by **7c**). The recovery of **7c** was compared to the production of **4a** to determine turnover numbers.

Turnover numbers and the corresponding frequency, f, of hydrogen peroxide formation with tellurapyrylium catalysts are compiled in Table V. Quantum yields for scavenging of singlet oxygen from self-sensitized generation and quantum yields for photochemical loss of catalyst for dye **7c** were determined in 99% methanol, 50% methanol, and water. Quantum yields for photochemical loss of catalyst were similar in all three solvents. For dyes **7a**, **7b**, **8a**, and **11**, turnover numbers were determined in 99% methanol. The monomethine dyes **8** and **11** were lost more rapidly than the trimethine dyes **7**. For the dyes **8** and **11**, the quantum yields for photochemical loss of catalyst at 1.0×10^{-5} M (2.5×10^{-5} and 3.1×10^{-5}, respectively) are nearly identical to the quantum yields for scavenging of singlet oxygen from self-sensitized generation (3.8×10^{-5} and 5.0×10^{-5}, respectively) in 99% methanol. For the trimethine dyes **7** at 1.0×10^{-5} M in 99% methanol, the quantum yields for scavenging of singlet oxygen from self-sensitized generation (3.1×10^{-5} for **7a**, 3.4×10^{-5} for **7b**, and 9.5×10^{-5} for **7c**) are essentially 1 order of magnitude larger than the quantum yields for photochemical loss of catalyst (2.7×10^{-6} for **7a**, 6.5×10^{-6} for **7b**, and 1.1×10^{-5} for **7c**).

In 50% methanol and in water, the scavenging of singlet oxygen from self-sensitized generation by **7c** is far more efficient than in 99% methanol with k(ox) being 2 orders of magnitude larger than in 99% methanol (Table V). Photochemical loss of catalyst is similar in the three systems, with quantum yields at 1.0×10^{-5} M **7c** of 5.5×10^{-5} in water, 3.7×10^{-5} in 50% methanol, and 1.1×10^{-5} in 99% methanol. The net result is an increase in turnover number with increasing water concentration.

The quantum yield for hydrogen peroxide generation is quite sensitive to solvent because of the effect of solvent on the rate of reaction of singlet oxygen with catalyst. At 298 K, the value of k(ox) for **7c** decreases from 8.0×10^8 M^{-1} s^{-1} in water to 1.8×10^8 M^{-1} s^{-1} in 50% aqueous methanol to 9.0×10^6 M^{-1} s^{-1} in 99% methanol with corresponding quantum yields for hydrogen peroxide production of 5.5×10^{-3}, 1.2×10^{-3}, and 9.5×10^{-5}, respectively.

The thermal component of Scheme II determines the rate at which hydrogen peroxide is produced. An initial steady-state concentration of dihydroxytellurane is reached photochemically followed by a slower change to an equilibrium concentration of catalyst, dihydroxytellurane, and hydrogen peroxide. The first-order rate constants (k_1) for decomposition of the dihydroxytelluranes are sensitive to solvent, as are the second-order rate constants (k_2) for the reaction of hydrogen peroxide with tellurapyrylium catalyst. Values of k_1 for dihydroxytellurane **5c** vary by 3 orders of magnitude from water to 99% methanol.[3] While k(ox) and k_2 increase with increasing water concentration k_1 decreases, minimizing the utility of the process shown in Scheme II.

Direct Oxidation with Dihydroxytelluranes Generated Photochemically. A far more efficient use of the scavenging of singlet oxygen from self-sensitized generation by tellurapyrylium dyes would be the direct use of the dihydroxytelluranes as oxidants as they are formed. As shown above, dihydroxytelluranes formed from the tellurapyrylium catalyst via the oxidative addition of hydrogen peroxide oxidize leucodyes **3** to **4** at a rate much greater than the reductive elimination of hydrogen peroxide from the dihydroxytellurane. At 298.0 ± 0.1 K in water (pH 6.8), **3a** and **3b** are oxidized by **5c** with second-order rate constants of $>10^3$ M^{-1} s^{-1}. At 1.0×10^{-6} M in **7c** and 1.0×10^{-4} M in **3**, the observed pseudo-first-order rate constants for the appearance of **4** from oxidation with photochemically generated **5c** in air-saturated aqueous solution (via irradiation of **7c** with filtered 630–850-nm light from a quartz–halogen source) is approximately 4×10^{-2} s^{-1}, which is much larger than k_1 for the reductive elimination of hydrogen peroxide in water. The final concentrations of **4a** of 8.0×10^{-5} M and of **4b** of 7.5×10^{-5} M, after 150 s or irradiation, correspond to turnover numbers of 80 and 75 in distilled water, respectively.

Tellurapyrylium dyes **7a** and **7b** (1.0×10^{-6} M) show similar behavior upon irradiation in air-saturated aqueous solutions of **3a** (1.0×10^{-4} M). Irradiation with filtered 630–850-nm light for 300 s gave complete oxidation of **3a** to **4a** (1.0×10^{-4} M) with each dye, corresponding to turnover numbers of ≥100.

Similar behavior is observed in 99% methanol. At an initial concentration of 3.0×10^{-6} M, **7c** will oxidize 1.56×10^{-4} M **3a** (initially 10^{-3} M) to **4a** upon irradiation (900 s) before the catalyst is consumed in air-saturated 99% methanol (Figure 1). Similarly, at an initial concentration of 1.0×10^{-6} M, **7c** will oxidize 5.13×10^{-5} M **3b** (initially 10^{-3} M) to **4b** upon irradiation before the catalyst is consumed in air-saturated 99% methanol. These values represent turnover numbers of >50 for **7c** in the photochemical reaction. These turnover numbers are greater than those observed for the generation of hydrogen peroxide in 99% methanol.

The ability of tellurapyrylium dyes to function as two-electron catalysts for the oxidation of leucodyes **3** is sum-

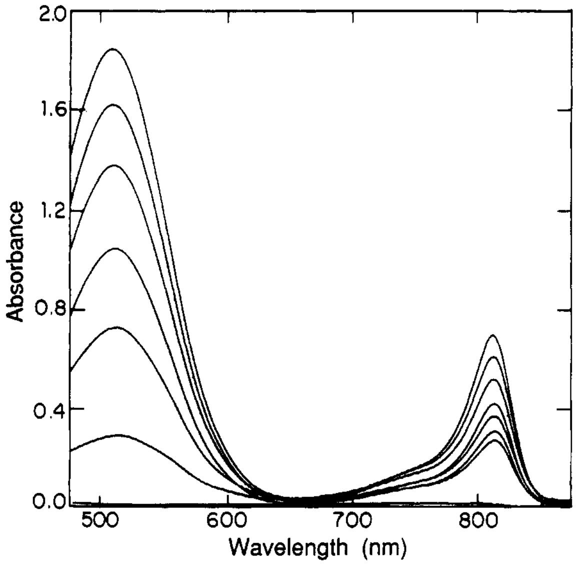
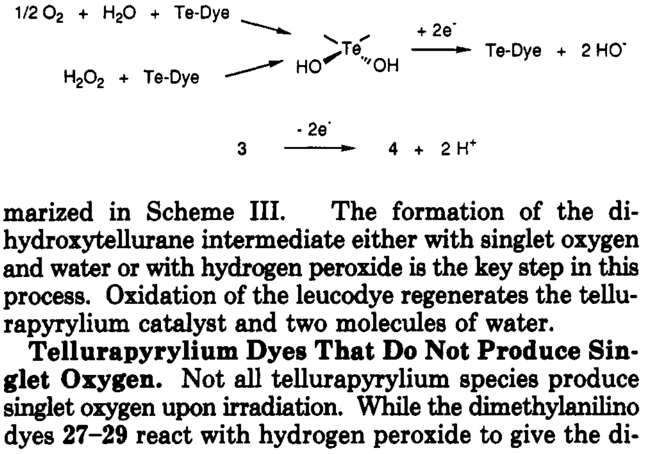


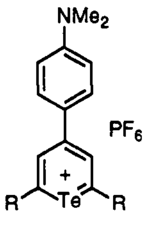
Figure 1. Photochemical oxidation of **3a** to **4a** in 99% aqueous methanol upon irradiation of **7c** with filtered light (630–850 nm) from a quartz–halogen source. The irradiation was stopped approximately every 60 s to generate the absorption curves shown (0–360 s), with the 515-nm absorption increasing with time and the 810-nm absorption decreasing with time. After 900 s, the optical density at 515 nm was 7.02 (measured by 10-fold dilution; curve not shown). The blank trace was for leucodye **3a** in air-saturated 99% aqueous methanol irradiated for 1200 s without catalyst.

Scheme III

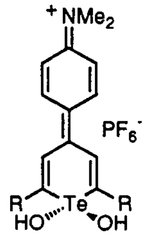


marized in Scheme III. The formation of the dihydroxytellurane intermediate either with singlet oxygen and water or with hydrogen peroxide is the key step in this process. Oxidation of the leucodye regenerates the tellurapyrylium catalyst and two molecules of water.

Tellurapyrylium Dyes That Do Not Produce Singlet Oxygen. Not all tellurapyrylium species produce singlet oxygen upon irradiation. While the dimethylanilino dyes **27–29** react with hydrogen peroxide to give the di-



27, R=H
28, R=*tert*-Bu
29, R=Ph



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hydroxytelluranes **30** as products of oxidative addition, attempts to generate species **30** via scavenging of singlet oxygen from self-sensitized generation in water or in aqueous methanol with these dyes were unsuccessful. Quantum yields for singlet oxygen generation in these systems were ≤0.0005 and suggest that dyes whose chromophores are charge transfer in nature will not produce significant yields of singlet oxygen. Furthermore, these dyes would not be practical for light-to-chemical energy storage schemes.

Summary and Conclusions

The two-electron shuttle between tellurium(II) and tellurium(IV) states can be exploited synthetically via reaction of the tellurium(IV) state with an oxidizable substrate. While hydrogen peroxide is a kinetically poor oxidant for substrates such as leucodyes **3** and aromatic thiols, dihydroxytelluranes (produced via oxidative addition of hydrogen peroxide across the tellurium atom of tellurapyrylium dyes) oxidize these substrates many orders of magntidue more rapidly. Upon reduction, the dihydroxytelluranes regenerate the tellurapyrylium species, allowing tellurapyrylium dyes to function as effective catalysts for hydrogen peroxide oxidations.

The rate accelerations of tellurapyrylium dyes are large with k_{cat} for dyes **7** being $>10^4$ for oxidations of leucodyes **3**. Turnover numbers are also >300. These values can be placed in proper perspective by comparison to those of the enzyme HRP. With HRP, the oxidations of leucodyes **3** to **4** are accelerated with k_{cat} $>10^9$ and with turnover numbers of $>10^6$.

Neutral organotellurium(II) species are not effective as catalysts for utilizing hydrogen peroxide as an oxidant. The reduction potentials of dihydroxytelluranes generated from tellurapyrylium dyes are several hundred millivolts more positive than those generated from neutral tellurium(IV) species. Thermodynamic arguments would suggest that the positively charged dihydroxytelluranes should be stronger oxidants than neutral dihydroxytelluranes.

Dihydroxyselenanes and dihydroxysulfuranes should be similar to the dihydroxytelluranes as oxidants in terms of reduction potentials. The oxidation of thiophenol to phenyl disulfide with a stoichiometric amount of a selenium(IV) species has been recently described.[21] However, the second-order rate constants for the addition of hydrogen peroxide to thiapyrylium dye **20** and to selenapyrylium dye **21** are both $\sim 10^{-4}$ less than those measured for tellurapyrylium dye **7c**. Kinetically, thiapyrylium and selenapyrylium dyes would be expected to have k_{cat} values at least 4 orders of magnitude smaller than the corresponding tellurapyrylium compounds for hydrogen peroxide oxidations. This is observed.

The heavy atom effect of tellurium gives high quantum yields for triplet formation and, as a consequence, for singlet oxygen generation.[8] The tellurium atoms of tellurapyrylium dyes react rapidly with singlet oxygen in the presence of water to produce dihydroxytelluranes with rate constants that vary between 9×10^6 M^{-1} s^{-1} in 99% methanol and 8×10^8 M^{-1} s^{-1} in water. The dihydroxytelluranes generated in this manner can be used as oxidants for substrates such as leucodyes **3**. The dihydroxytelluranes also form hydrogen peroxide via a thermal process which regenerates the starting tellurapyrylium dyes.

The scavenging of singlet oxygen by tellurapyrylium compounds is far more efficient than scavenging of singlet oxygen by thiapyrylium and tellurapyrylium compounds. In 50% aqueous methanol, $k(^1O_2)$ is 1.8×10^8 M^{-1} s^{-1} for tellurapyrylium compound **7c** but only 9.0×10^6 M^{-1} s^{-1} for thiapyrylium dye **20** and 5.0×10^6 M^{-1} s^{-1} for selenapyrylium dye **21** (Table II).[8] In 50% aqueous methanol at 298 K and at 1×10^{-5} M dye, the quantum yield of scavenging of singlet oxygen from self-sensitized generation

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(21) Detty, M. R.; McKelvey, J. M.; Luss, H. R. *Organometallics* **1988**, *7*, 1131–1147.

is 1.2×10^{-3} for tellurapyrylium dye **7c** but is less than or equal to 3.7×10^{-6} for thiapyrylium dye **20** [$\Phi(^1O_2) = 0.007$][8b] and 7.6×10^{-6} for selenapyrylium dye **21** [$\Phi(^1O_2) = 0.013$],[8b] using eq 6 and assuming a value of *f* of 1.00 (perfect catalyst). Again, the tellurapyrylium dyes are at least 3 orders of magnitude more efficient than corresponding thiapyrylium and selenapyrylium dyes at reducing oxygen in the presence of water to give either dihydroxychalcogenuranes or hydrogen peroxide.

Tellurapyrylium dyes hold promise as two-electron shuttles for a variety of oxidants and as vehicles for solar energy storage. The coupling of the photochemical generation of dihydroxytelluranes with other reactants oxidizable by dihydroxytelluranes might lead to the development of fuel cells based on this chemistry. Thiapyrylium compounds and selenapyrylium compounds are much less promising since they are orders of magnitude less reactive with either hydrogen peroxide or singlet oxygen.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a General Electric QE-300 spectrophotometer. UV–visible–near-infrared spectra and spectroscopic kinetic runs were recorded on a Perkin-Elmer Lambda 9 spectrophotometer equipped with constant-temperature cell holders. Infrared spectra were recorded on a Beckman IR 4250 instrument. Mass spectra were recorded on a DuPont 21-491 instrument equipped for field desorption. Microanalyses were performed on a Perkin-Elmer 240 C, H, and N analyzer. Methanol was distilled from magnesium turnings onto glass and was stored under argon. Thiophenol was used as received from Aldrich. Methanol-d_4 was used as received from Aldrich. Compounds **7a–c**, **20**, and **21** were prepared according to ref 8b. Compounds **8**, **13**, **15**, and **28** were prepared according to ref 21. Compound **11**, **12**, **14**, and **29** were prepared according to ref 22. Compound **16** was prepared according to ref 23. Compound **17** was prepared according to ref 24. Compound **18** was prepared according to ref 25.

Photolyses were carried out with light from a 500-W tungsten filament lamp filtered through appropriate narrow-band (10 nm) interference filters and cutoff filters. Irradiation intensity was monitored with an EG&G 450-1 radiometer calibrated vs a standard thermopile. Reinecke's salt actinometry provided a calibration check.[26]

Electrochemical Procedures. A Princeton Applied Research Model 173 potentiostat/galvanostat and a Model 175 Universal Programmer were used for the electrochemical measurements. The working electrode for cyclic voltammetry was a platinum disk electrode (diameter, 1 mm) obtained from Princeton Applied Research. The working electrode for bulk coulometry was a platinum gauze basket. The auxiliary electrode was a platinum wire. The reference electrode for both the cyclic voltammetry and the coulometry experiments was a AgCl-saturated calomel electrode.

All samples were run in J. T. Baker HPLC-grade dichloromethane or acetonitrile that had been stored over Kodak-type 3A molecular sieves. Electrometric-grade tetra-*n*-butylammonium fluoroborate (Southwestern Analytical Chemicals, Inc.) was recrystallized from ethyl acetate–ether and then dried overnight at 80 °C before it was used as supporting electrolyte at 0.2 M concentration. Argon was used for sample deaeration.

Oxidation of Leucodyes 3 with Hydrogen Peroxide in the Presence of Catalysts. Stock solutions of leucodyes **3** at 1.0×10^{-4} M were prepared in pH 6.8 phosphate buffer with 0.010 M hydrogen peroxide. Stock solutions of the catalyst were prepared in methanol at 1.0×10^{-3} M concentrations. The leucodye solutions were placed in 1-cm^2 quartz cuvettes at volumes of 2.700–2.997 mL in the constant-temperature cell holders maintained at 298.0 ± 0.1 K. Appropriate volumes of the catalyst solutions (0.0030–0.300 mL) were added to give 3.00 mL of solution. The absorbance at λ_{max} of the dye **4** was monitored as a function of time. The pseudo-first-order rate constants obtained werre divided by hydrogen peroxide concentration to give second-order rate constants. Values given in Table III are the average of duplicate runs. Blank runs were obtained by monitoring the appearance of the absorbance of **4** from the stock solutions of leucodye **3** and hydrogen peroxide.

Oxidation of Leucodyes 3 with 5c. Stock solutions of leucodyes **3** at 2.0×10^{-4} M were prepared in pH 6.8 phosphate buffer. Stock solutions of **7c** were prepared in distilled water at 2.0×10^{-5} M concentrations. A 1.00-mL aliquot of the stock solution of **7c** in a 1-cm^2 quartz cuvette was irradiated with 630–850-nm filtered light from a quartz–halogen source until complete conversion of **7c** to **5c**. The resulting solution of **5c** was brought to 298.0 ± 0.1 K and a 1.00-mL aliquot of the solution of leucodye **3**, at 298.0 ± 0.1 K, was added to the quartz cuvette. The absorbance at λ_{max} of the dye **7c** was monitored as a function of time. The pseudo-first-order rate constants obtained were divided by the concentration of leucodye **3** to give second-order rate constants. Half-lives were on the order of 5 s, which correspond to pseudo-first-order rate constants of $>1 \times 10^{-1}$ s^{-1} and apparent second-order rate constants of $>1 \times 10^3$ M^{-1} s^{-1}.

Oxidation of Thiophenol with Hydrogen Peroxide. A stock solution of 0.2932 g of thiophenol in 10.0 mL of methanol-d_4 (0.267 M) was prepared. Stock solutions of the catalysts [$(2.5–3.0) \times 10^{-3}$ M] were prepared in methanol-d_4. Samples were prepared by placing 0.375-mL aliquots of the stock solution of thiophenol in an NMR tube and diluting with stock solution of catalyst and methanol-d_4 to a volume of 0.750 mL. To this solution was added 0.250 mL of 30% hydrogen peroxide, giving a final peroxide concentration of 2.4 M and a final thiophenol concentration of 0.100 M. The rate of formation of phenyl disulfide was monitored by integrating the ortho protons of phenyl disulfide (δ 7.52) with the remainder of the aromatic protons (δ 7.14–7.38) at 296.3 ± 0.1 K. The pseudo-second-order rate constant obtained was divided by 2.4 M to give the apparent third-order rate constants. The value given ($\sim 3 \times 10^{-4}$ M^{-2} s^{-1}) is the average of four runs.

Oxidation of Thiophenol with 5c. A stock solution of 0.0220 g of thiophenol in 100.0 mL of methanol (0.00200 M) was prepared. Stock solutions of **7c** were prepared in 50% methanol at 2.0×10^{-5} M concentrations. A 1.00-mL aliquot of the stock solution of **7c** in a 1-cm^2 quartz cuvette was irradiated with 630–850-nm filtered light from a quartz–halogen source until complete conversion of **7c** to **5c**. The resulting solution of **5c** was brought to 298.0 ± 0.1 K, and a 1.00-mL aliquot of the solution of thiophenol, at 298.0 ± 0.1 K, was added to the quartz cuvette. The absorbance at λ_{max} of the dye **7c** was monitored as a function of time at 298.0 ± 0.1 K. The pseudo-first-order rate constants obtained [$(5.2 \pm 0.2) \times 10^{-2}$ s^{-1}] were divided by the square of the concentration of thiophenol to give the apparent third-order rate constants ($>5 \times 10^4$ M^{-2} s^{-1}).

Preparative Oxidations of Aromatic Thiols with Hydrogen Peroxide and Tellurapyrylium Catalysts. The aromatic thiol (0.009 15–0.010 02 mol) and catalyst (0.015–0.10 mmol) were placed in a 100.0-mL volumetric flask and were diluted to the mark with 2.4 M hydrogen peroxide in 75% methanol (prepared by diluting 125 mL of 30% hydrogen peroxide to 500.0 mL with methanol). After 0.5 h at ambient temperature, the reaction mixture was diluted with an equal volume of water. For phenyl disulfide and *p*-methoxyphenyl disulfide, the crystalline materials were collected by filtration, washed with water (3 × 50 mL), and dried under vacuum to give the disulfides, mp 61–62 °C for phenyl disulfide and mp 76–78 °C for *p*-methoxyphenyl disulfide. For *p*-fluorophenyl disulfide, the reaction mixture was diluted with 300 mL of water and the products were extracted with dichloromethane (3 × 75 mL). The combined extracts were washed with brine, dried over sodium sulfate, concentrated, and dried under vacuum to give the disulfide as a viscous, colorless oil. For **7c**, 10.2 ± 0.1 mg of catalyst (1.5×10^{-5} mol) was added to 1.008 ± 0.003 g (0.009 98 mol) of thiophenol yielding 0.988 ± 0.007 g (97.8%) of phenyl disulfide. For **13**, 7.1 ± 0.1 mg (1.4×10^{-5}

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mol) of catalyst was added to 1.099 ± 0.002 g (0.0997 mol) of thiophenol yielding 1.055 ± 0.010 g (96.9%) of phenyl disulfide. Values given are the average of duplicate runs. For *p*-methoxybenzenethiol, 34.1 of **7c** (5.0×10^{-5} mol) was added to 1.702 g of the thiol (0.01000 mol) yielding 1.667 g (98.5%) of disulfide. For *p*-fluorobenzenethiol, 34.1 mg of **7c** was added to 1.462 g (0.01000 mol) of thiol yielding 1.410 g (97.1%) of disulfide.

Oxygen Electrode Studies. The concentration of oxygen in the photolyzed solutions of **7** was monitored using an OM-1 biological oxygen meter connected to a microprobe (Microelectrodes, Inc., Londonderry, NH). The concentration of oxygen in the solutions was controlled by bubbling air through the solvent prior to irradiation or by bubbling and oxygen–nitrogen mixture produced using an Oxyreducer (Reming Bioinstruments, Redfield, NY) as described previously.[27] Oxygen consumption by irradiation of the dyes **7** at 20, 5, and 3% oxygen were similar at all three concentrations. For 5.0×10^{-5} M **7a**, oxygen concentration was lowered by $(2.6 \pm 0.3) \times 10^{-5}$ M; for 6.2×10^{-5} M **7b**, oxygen concentration was lowered by $(2.2 \pm 0.3) \times 10^{-5}$ M; for 9.3×10^{-5} M **7c**, oxygen concentration was lowered by $(4.0 \pm 0.3) \times 10^{-5}$ M. These values represent the average of five independent runs.

Determination of Second-Order Rate Constants for the Oxidative Addition of Hydrogen Peroxide to 7, 13, 20, and 21. Stock solutions of hydrogen peroxide at 1.0, 0.10, and 0.010 M were prepared in water by dilution of 30% hydrogen peroxide. Stock solutions of 1.0 M hydrogen peroxide in 90% methanol were prepared by a 10-fold dilution of 30% hydrogen peroxide with methanol. Stock solutions of 0.10 M in hydrogen peroxide were prepared by a 10-fold dilution with methanol of the 1.0 M aqueous hydrogen peroxide. Stock solutions of 0.10 M hydrogen peroxide in 75% methanol were prepared by dilution of 0.40 M aqueous hydrogen peroxide. Stock solutions of **7**, **20**, and **21** at 1.0×10^{-3} M in methanol were prepared. A 0.030-mL aliquot of the dye solution was added to 3.00 mL of the peroxide solution. The decrease in absorbance of the dye was monitored as a function of time. The pseudo-first-order rate constants obtained were divided by hydrogen peroxide concentration to give the apparent second-order rate constants. Values given in Table II are the average of duplicate runs.

Catalytic Conversion of Oxygen and Water to Hydrogen Peroxide via Self-Sensitized Scavenging of Singlet Oxygen with Tellurapyrylium Dyes. A 1×10^{-5} M solution of tellurapyrylium dye in 99% methanol was irradiated in a 1-cm^2 quartz cuvette for 2000 s. The absorbances at λ_{max} of both the reduced tellurapyrylium dye and the dihydroxytellurane were measured. These absorbances were used to calculate the concentration of tellurapyrylium dye remaining in either the Te(II) or Te(IV) oxidation state. A 1.00-mL aliquot of the irradiated solution was diluted with 0.97 mL of distilled water, 1.00 mL of pH 6.00 phosphate buffer, and 1.00 mL of a 4×10^{-4} M solution of leucodye **3a** in methanol in a 1-cm^2 quartz cuvette. The resulting solution was placed in a spectrophotometer at 298.0 K, and 0.030 mL of a 3×10^{-9} M solution of horseradish peroxidase was added. The final optical density at 515 nm (λ_{max} for **4a**, ϵ 31000 in 50% methanol) was determined. The concentration of hydrogen peroxide was calculated from the formation of **4a**. The turnover numbers were taken as the ratio of hydrogen peroxide produced over amount of catalyst lost. The values given in Table V are the average of 10 runs with deviations given at the 95% confidence limit.

A 9.32×10^{-6} M solution of **7c** in 50% aqueous methanol was irradiated for 2000 s in a 1-cm^2 quartz cuvette. The absorbances at λ_{max} of both the reduced tellurapyrylium dye and the dihydroxytellurane were measured. These absorbances were used to calculate the concentration of tellurapyrylium dye remaining in either the Te(II) or Te(IV) oxidation state. A 1.00-mL aliquot of the irradiated solution was diluted with 0.47 mL of distilled water, 0.500 mL of methanol, 1.00 mL of pH 6.00 phosphate buffer, and 1.00 mL of a 4×10^{-4} M solution of leucodye **3a** in methanol in a 1-cm^2 quartz cuvette. The resulting solution was placed in a spectrophotometer at 298.0 K, and 0.030 mL of a 3×10^{-9} M solution of horseradish peroxidase was added. The final optical density at 515 nm (λ_{max} for **4a**, ϵ 31000 in 50% methanol) was determined. The concentration of hydrogen peroxide was calculated from the formation of **4a**. The value given in Table V is the average of six independent runs with deviations given at the 95% confidence limit.

A 1.05×10^{-5} M solution of **7c** in distilled water was irradiated for 3600 s in a 1-cm^2 quartz cuvette. The absorbances at λ_{max} of both the reduced tellurapyrylium dye and the dihydroxytellurane were measured. These absorbances were used to calculate the concentration of tellurapyrylium dye remaining in either the Te(II) or Te(IV) oxidation state. A 1.00-mL aliquot of the irradiated solution was diluted with 1.00 mL of methanol, 0.97 mL of pH 6.00 phosphate buffer, and 1.00 mL of a 4×10^{-4} M solution of leucodye **3a** in methanol in a 1-cm^2 quartz cuvette. The resulting solution was placed in a spectrophotometer at 298.0 K, and 0.030 mL of a 3×10^{-9} M solution of horseradish peroxidase was added. The final optical density at 515 nm (λ_{max} for **4a**, ϵ 31000 M^{-1} in 50% methanol) was determined. The concentration of hydrogen peroxide was calculated from the formation of **4a**. The value given in Table V is the average of six runs with deviations given at the 95% confidence level.

Photochemical Oxidations of Leucodyes 3 in the Presence of 7c. Stock solutions of 1.0×10^{-3} M **3a** and **3b** were prepared in 99% methanol. Stock solutions of 1.0×10^{-4} M **3a** and **3b** were also prepared in water (pH 6.8 from phosphate buffer). Samples (3.00 mL) of these solutions were placed in 1-cm^2 quartz cuvettes. To these solutions were added appropriate aliquots of the 1.0×10^{-3} M **7c** in 99% methanol. The solutions were irradiated until consumption of catalyst as determined spectrophotometrically. The photolyzed samples were diluted to 25.0 mL, and the optical density for λ_{max} of **4** was measured. The final concentration of dye **4** in the cuvette was determined (ϵ 45000 M^{-1} for **4a**, ϵ 55000 M^{-1} for **4b** in 99% methanol; ϵ 30000 M^{-1} for **4a**, ϵ 40000 M^{-1} for **4b** in pH 6.8 buffer).

Rate Constants for the Reaction of Tellurapyrylium Dyes 8 and 11 with Singlet Oxygen. Rate constants for reaction between dye **8** or **11** and singlet oxygen were measured by photolyzing methanol solutions containing a sensitizer with a known quantum yield for singlet oxygen generation and the dye **8** or **11**. The dye concentration was sufficiently low to have negligible effect on the decay of singlet oxygen. The specifics of the procedure using rose bengal as sensitizer are described in ref 8b (p 3854). The uncertainty in the value of **11** was largely due to photolytic fade in the dye.

Preparation of 4-(*p*-(*N*,*N*-Dimethylamino)phenyl)tellurapyrylium Hexafluorophosphate (27). A mixture of *p*-bromo-*N*,*N*-dimethylaniline (0.60 g, 3.0 mmol) and magnesium turnings (0.12 g, 5.0 mg-atom) in 10 mL of anhydrous THF was heated at reflux for 1.5 h under argon. The reaction mixture was cooled to ambient temperature and Δ-4*H*-tellurapyran-4-one[28] (0.312 g, 1.50 mmol) in 5 mL of anhydrous THF was added dropwise via syringe. The reaction mixture was heated at reflux for 1 h and then poured into 50 mL of cold, 10% HPF_6. The purple solid was collected by filtration, washed with water (4 × 10 mL) and ether (4 × 10 mL), and dried. The solid was recrystallized from acetonitrile and an equal volume of ether to give 0.486 g (71%) of **27** as a purple-black solid: mp 220–221 °C dec; ^{1}H NMR (CD_2Cl_2) δ 10.60 (d, 2 H, J = 11.6 Hz), 8.80 (d, 2, H, J = 11.6 Hz), 8.08 (AA′BB′, 2 H), 6.93 (AA′BB′, 2 H), 3.24 (s, 6 H); λ_{max} (CH_2Cl_2) 628 nm (ϵ 80000 M^{-1}). Anal. Calcd for $C_{13}H_{14}NTe{\cdot}PF_6$: C, 34.18; H, 3.09; N, 3.07. Found: C, 34.64; H, 3.22; N, 3.17.

OM910713D

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