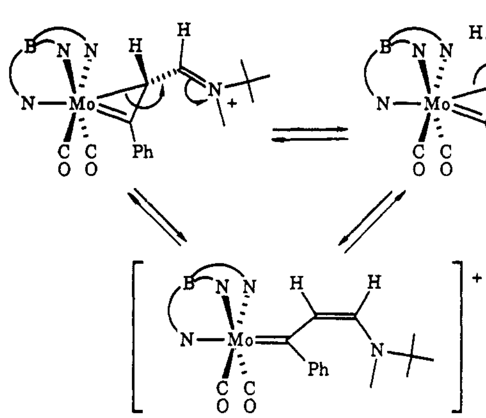
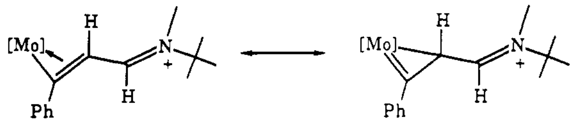
Scheme VIII



1.295 (8) Å) lie between values expected for single and double bonds, and suggest extensive π-delocalization in this fragment. The C(3)–C(4)–C(5)–N(6) torsion angle of 173.0 (8)° supports this view. The C(3)–C(4) bond distance of the vinyl is actually longer than that of C(4)–C(5), which is formally a single bond. Bond lengthening in the vinyl group can be understood by examining resonance structures of the compound.



The addition of hydride to 9 to give the neutral η^2-vinyl complex 10 is typical chemistry for iminium salts.[44] Compound 10 is generated as a racemic mixture of enantiomers, which show no fluxionality on the NMR time scale. The electronic ambiguity present in 9 due to potential positive charge localization at either metal or nitrogen is absent in 10.

Conclusion

Electrophilic addition to anionic molybdenum isocyanide derivatives is dominated by direct attack at nitrogen to form carbyne products, but alkylation at the metal followed by insertion can form η^2-iminoacyl complexes in some cases. The aminocarbyne products, formed in high yield for methyl and phenyl isocyanide reagents, can be protonated in the presence of phenylacetylene to form η^2-vinyl complexes via alkyne insertion into the transient metal–carbene bond. Hydride addition to the free iminium carbon generates a neutral η^2-vinylamine complex. The η^2-iminoacyl complex accessible from the *tert*-butyl isocyanide reagent has been elaborated at the iminoacyl C_β position by a deprotonation/alkylation sequence.

Acknowledgment. We gratefully acknowledge the Department of Energy, Division of Chemical Sciences, for support of this research (Grant 85ER13430).

Supplementary Material Available: For 9, tables of anisotropic temperature factors, bond distances and angles, and calculated hydrogen positions as well as an ORTEP diagram of 9 with the complete atomic numbering scheme (5 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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Reaction Pathways of Telluroxide Equivalents. Reductive Elimination of Hydrogen Peroxide from Dihydroxytelluranes and Oxidation of Carbon via Intramolecular Transfer of Oxygen

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Dihydroxytelluranes 2 undergo a thermal reductive elimination of hydrogen peroxide to generate tellurapyrylium dyes 1 in 99% methanol, 90% methanol, 50% methanol, water, and phosphate-buffered saline (PBS). Temperature-dependent first-order rates of reaction were measured for the disappearance of **2d** in 99% methanol and 90% methanol. The reductive elimination was found to proceed in >95% yield in these solvents. The first-order rate constant for reductive elimination decreased with increasing water concentration, while $\Delta G^{\ddagger}$ increased from 13.9 kcal mol^{-1} in 99% methanol to 14.8 kcal mol^{-1} in 90% methanol. In PBS, temperature-dependent first-order rate constants were measured for **2b–d** at 310.0, 323.0, and 333.0 K. Values of $\Delta H^{\ddagger}$ of 21.3 ± 0.6, 20.5 ± 0.9, and 20.9 ± 0.1 kcal mol^{-1} were calculated for **2b–d**, respectively. Corresponding values for $\Delta S^{\ddagger}$ of 12 ± 2, 11 ± 3, and 10.9 ± 0.5 cal mol^{-1} K^{-1} were calculated for **2b–d**, respectively. The positive charge on species 2 leads to increased acidity of the hydroxyl protons with first $\mathrm{p}K_a$'s of −1.9 and −2.1 measured spectrophotometrically for **2c,d**, respectively, and second $\mathrm{p}K_a$'s of 7.8 and 7.7 for **2c,d**, respectively. The rate of disappearance of 2 was a function of pH. Over the pH range 4.24–7.37, where compounds 2 would be zwitterionic, fairly constant rates of disappearance were measured ($(2.3 \pm 0.2) \times 10^{-5}$ s^{-1}). At lower pH values, where 2 would be more fully protonated, the rate of disappearance of 2 increases as does the rate of appearance of 1. At a pH of 9.19, where the second acidic proton would be ionized, the rate constant for the disappearance of 2 is much larger. In PBS, a second reaction pathway is observed for **2b–d**. Tellurophene 7 is produced as the product of intramolecular oxidation of carbon with the oxygen of the tellurium(IV) species.

Many synthetic transformations have been devised that incorporate the higher oxidation states of the selenium atom (the selenoxide and selenone states) in organoselenium compounds. Perhaps the best studied of these transformations are elimination reactions of selenoxides to give olefins.[1] In other transformations, the selenoxide

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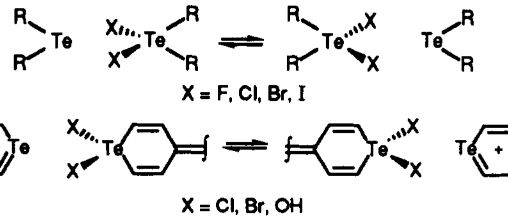
Scheme I

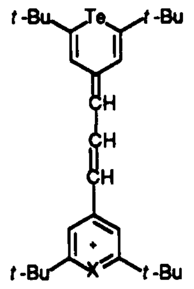


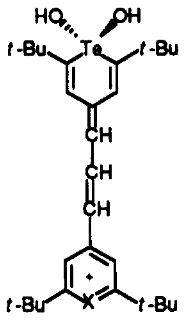
oxygen atom is transferred to a carbon atom as in [2,3]-sigmatropic rearrangements of allylic selenoxides to give allylic alcohols[1a,b,2] and Pummerer-like reactions of selenoxides to give alcohols.[3]

Similar reactions of higher oxidation states (corresponding telluroxide and tellurone states) of organotellurium compounds have been far fewer in number. Synthetic reactions of telluroxides have been limited to elimination reactions in which tellurones or tellurinic esters may be formed in situ and act as leaving groups.[4]

The chemistry of telluroxides and tellurones has been little explored. While certain diaryl telluroxides are stable as the telluroxide,[5] alkyl aryl telluroxides and dialkyl telluroxides add water to give dihydroxytelluranes.[6] While the basicity of the oxygen atom in the telluroxide group allows the use of diaryl telluroxides as catalysts for the aldol reaction,[5] the dihydroxytelluranes are nonpolar molecules that do not appear to undergo chemical reactions similar to those of the selenoxides.

In our studies of the tellurapyrylium dyes **1**, tellurium(IV) species **2** were prepared by the oxidative addition of hydrogen peroxide or singlet oxygen and water across a tellurium atom of dye **1**.[7] Dihydroxytelluranes **2** differ in structure from other dihydroxytelluranes reported in the literature[5,6] in that the tellurium(IV) center is linked via the carbon π-framework to a formal positive charge.


1a–d


2a–d

X = O (**a**), S (**b**), Se (**c**), Te (**d**)

Table I. n-Octanol/Water Partition Coefficients (P) and Spectral Properties of Tellurapyrylium Dyes 1 and Oxidized Dyes 2

compd	log P	$\lambda_{max}(H_2O)$, nm	log ϵ
1a	2.41	700	5.27
1b	2.26	755	5.02
1c	2.41	770	5.10
1d	2.02	810	5.22
2a	<−3.00	452.	4.69
2b	<−3.00	480	4.72
2c	<−3.00	502	4.74
2d	<−3.00	510	4.75

The chemistry and biochemistry of tellurium(IV) species such as **2** have been little investigated. It is known that tellurium(IV) species containing halide ligands are reduced to tellurium(II) species with loss of the halide ligands by use of mild reducing agents.[8] It is also known that tellurium(IV) species will exchange halide ligands with a tellurium(II) center, resulting in an interchange of oxidation states. As shown in Scheme I, tellurium–halogen exchange has been observed in both neutral[9] and positively charged[8a] species. Both first-order and second-order mechanisms have been observed in exchange reactions of this type.

The chemistry of dihydroxytelluranes **2** becomes biologically important due to the promise tellurapyrylium dyes of structure **1** show as photosensitizers[10] for photodynamic therapy (PDT), a recently developed technique for the treatment of cancer.[11] In vitro studies have demonstrated that tellurapyrylium dyes **1** are oxidized to dihydroxytelluranes **2** in the mitochondria of transformed cells when dyes **1** are exposed to near-infrared light.[10,12]

In this paper, some reactions of the tellurium(IV) species **2** in solution are described, which do not have precedent in the chemistry of selenoxides or sulfoxides. Compounds **2** are found to be dibasic acids, to undergo hydroxyl ligand exchange with tellurium(II) centers, to undergo reductive, thermal loss of hydrogen peroxide, and to undergo intramolecular transfer of oxygen from tellurium(IV) to an adjacent carbon center.

Results and Discussion

Preparation of Tellurium(IV) Species 2. Solutions of **2** in water or aqueous methanol were prepared in concentrations of up to 10^{-3} M via irradiation at 0 °C of air-saturated solutions of tellurapyrylium dyes **1**.[7] The tel-

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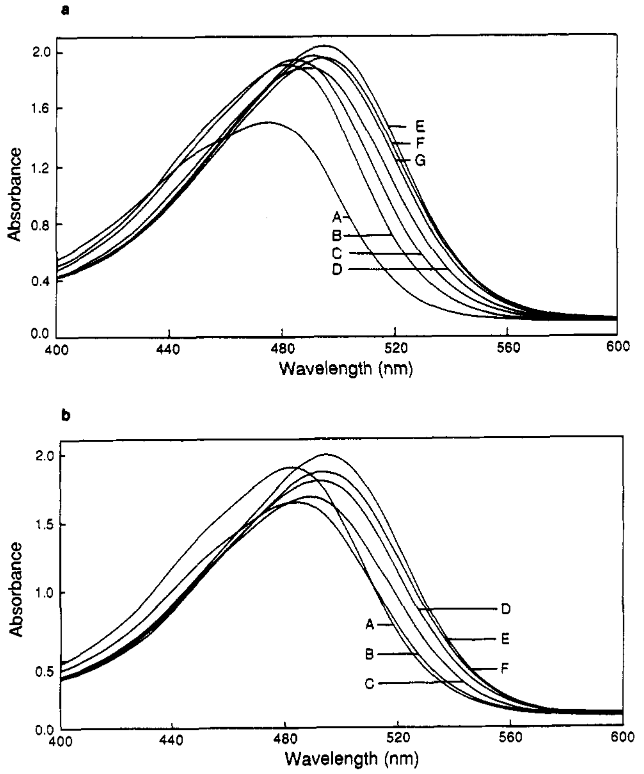


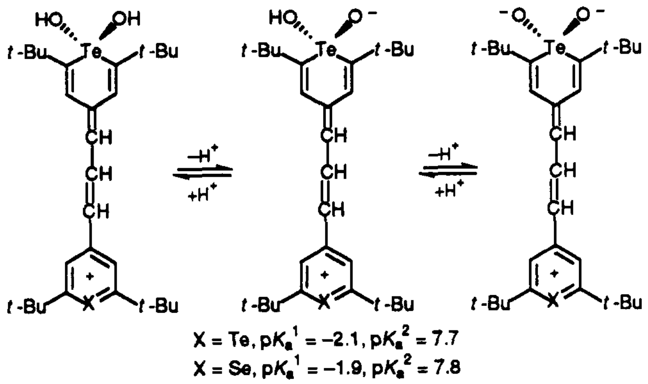
Figure 1. (a) Effect of pH on the absorption spectrum of **2c**: (A) pH 1.05; (B) pH 3.11; (C) pH 4.24; (D) pH 5.16; (E) pH 7.20; (F) pH 6.30; (G) pH 5.98. (b) Effect of pH on the absorption spectrum of **2d**: (A) pH 1.05; (B) pH 3.11; (C) pH 4.24; (D) pH 5.16; (E) pH 7.20; (F) pH 5.98.

lurapyrylium dyes **1** displayed isosbestic behavior upon irradiation to give **2** with conversions of greater than 99%.

In water or phosphate-buffered saline (PBS), trace amounts of the dyes **1** were removed from the aqueous layer by partitioning the photolysis reaction mixture between the aqueous solvent and *n*-octanol. As shown in Table I, values of log *P*, where *P* is the partition coefficient between *n*-octanol and water, differ by more than 5 orders of magnitude. The photooxidized dyes **2** are much more water-soluble than *n*-octanol-soluble (log $P < -3.0$) relative to dyes **1** (log $P \approx 2.0$).

The addition of excess hydrogen peroxide to solutions of tellurapyrylium dyes **1** (0.1–1.0 M) in methanol or a mixture of dichloromethane and methanol at 0 °C gave the oxidized dyes **2** in several hundred milligram quantities. The reaction mixtures were concentrated in vacuo at 0 °C or lower to give the products as dark maroon powders in 95–98% purity.

Scheme II



Stock solutions of compounds **2** (≤5 mM) were prepared by saturating a methanol solution with tellurapyrylium dye **1** (~1 mmol/4 mL) and adding approximately 0.9 equiv of hydrogen peroxide at 0 °C. The reaction mixture was diluted with cold water or PBS to the desired concentration. Unreacted tellurapyrylium dye **1** was removed via filtration followed by extraction of the filtrate with dichloromethane or *n*-octanol.

Acidities of the Hydroxyl Protons in Compounds 2. The pH of 10^{-4} M aqueous solutions of tellurapyrylium dyes **1** decreased during irradiation as **1** was converted to **2**. Upon complete oxidation of **1** to **2**, the pH of the reaction mixture was approximately 4. The decrease in pH suggested the formation of a strongly acidic product from the photolysis.

Titration of 10^{-3} M solutions of **2c** or **2d** (initial pH of 3) with sodium hydroxide gave pK_a's of 7.8 and 7.7 for **2c**,**d**, respectively, for what is presumably a second acidic proton. As shown in Figure 1a for **2c** and in Figure 1b for **2d**, the absorption spectra of tellurium(IV) species **2** are quite sensitive to the pH of the solvent. From the changes in the absorption spectra, the first pK_a's for **2c**,**d** were calculated to be −1.9 and −2.1, respectively.[13] In aqueous

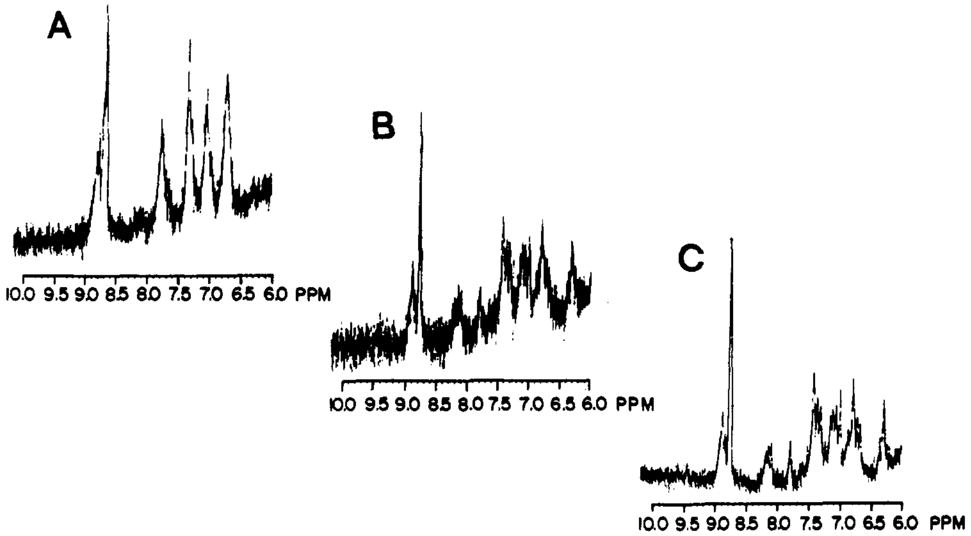


Figure 2. Variable-temperature ^{1}H NMR studies of an equimolar mixture of **1c** and **2c** in 50% D_2O-CD_3OD: (A) T = 294 K; (B) T = 273 K; (C) T = 253 K.

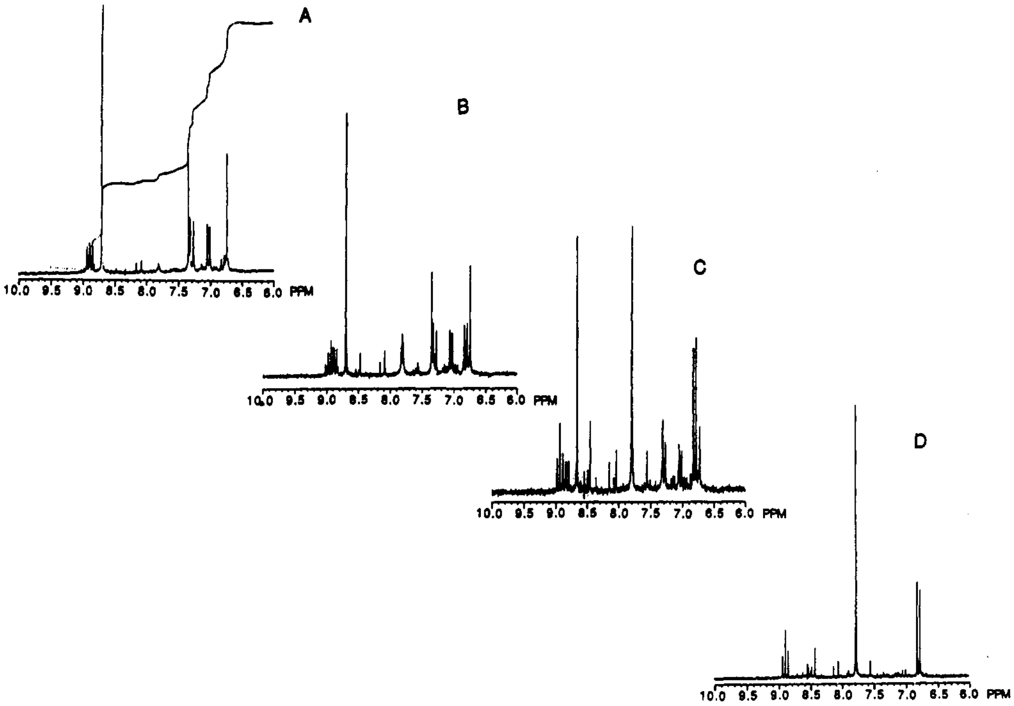


Figure 3. ^{1}H NMR spectra of a CD_3OD solution of **2d** at 310 K: (A) $t = 0$; (B) $t = 900$ s; (C) $t = 1800$ s; (D) $t = 7200$ s.

solvent, complete dissociation of the first acidic proton would be expected for compounds 2. The dibasic character of compounds 2 is summarized in Scheme II.

Tellurium-Ligand Exchange with Hydroxyl Ligands. Evidence for tellurium-ligand exchange was found in the variable-temperature ^{1}H NMR spectra of mixtures of **1c** and **2c**. As shown in Figure 2A, complete coalescence of signals is observed in the olefinic region for an equimolar mixture of **1c** and **2c** at ambient temperature (294 K) in a 1:1 (by volume) mixture of deuterium oxide and methanol-d_4. The sample was cooled to 273 K in Figure 2B. Some separation of signals is observed. At 253 K in Figure 2C, both sets of olefinic signals are resolved for **1c** and **2c**. These results suggest that rapid exchange of ligands between tellurium(IV) centers in **2c** and tellurium(II) centers in **1c** occurs at higher temperatures and is responsible for the coalescence of signals observed by ^{1}H NMR spectroscopy.

Thermal Reaction of 2d in Methanol. A solution of **2d** in methanol-d_4 did not appear to be exchanging tellurium ligands between the two tellurium atoms of each molecule at a fast rate. As shown in Figure 3A, the well-resolved signals for **2d** show equivalency of the tellurapyrylium ring protons while the tellurapyranylidene unit containing the tellurium(IV) center displays two distinct olefinic singlets for the ring protons and three distinct resonances for the three protons of the trimethine bridge. Heating the sample to 310 K did not lead to rapid exchange of ligands between tellurium atoms of **2d**. Instead, reduction of the tellurium(IV) center occurred upon standing at 310 K to regenerate **1d** (Figure 3D).

The thermal conversion of **2d** to **1d** followed first-order kinetics, as monitored by variable-temperature ^{1}H NMR spectroscopy in methanol-d_4 at 303, 310, and 317 K. Values of the first-order rate constant at the three different temperatures were 3.0×10^{-4}, 5.6×10^{-4}, and 1.4×10^{-3} s^{-1}, respectively, which correspond to activation parameters of $\Delta H^{\ddagger} = 20 \pm 3$ kcal mol^{-1} and $\Delta S^{\ddagger} = 16 \pm 2$ cal K^{-1} mol^{-1}.

Table II. Thermal Rates of Reduction and Activation Parameters for 2d in Aqueous Methanol[a]

	10^4k, s^{-1}	
T, K	99% MeOH[b]	90% MeOH[c]
296.0	23.8 ± 0.6	4.52 ± 0.03
303.0	53.8 ± 2.5	12.7 ± 0.2
310.0	110.0 ± 0.5	24.7 ± 0.5
317.0	203.0 ± 2.0	43.7 ± 0.4
324.0		91.0 ± 2.0
331.0		144.0 ± 0.6

[a] Average of duplicate runs agreeing in value within 4%. [b] $\Delta H^{\ddagger} = 18.5 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = 15.6 \pm 0.1$ cal K^{-1} mol^{-1}, $E_a = 19.1 \pm 0.5$ kcal mol^{-1}, $A = 24.40 \pm 0.04$. [c] $\Delta H^{\ddagger} = 18.3 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = 11.9 \pm 0.2$ cal K^{-1} mol^{-1}, $E_a = 18.9$ kcal mol^{-1}, $A = 24.45 \pm 0.08$.

Kinetic Analysis of the Formal Reductive Elimination of Hydrogen Peroxide from Compound 2d in Aqueous Methanol. The production of tellurapyrylium dyes 1 from heating solutions of 2 is formally a reductive elimination of hydrogen peroxide from the tellurium(IV) center in compounds 2. There is little precedent for reactions of this type at a chalcogen center in the literature. The closest examples are found in first-order tellurium–halogen exchange reactions.[6a,7] In acetonitrile, the dibromide analogue of **2d** was found to follow first-order behavior with respect to tellurium–bromine exchange. For this reaction, $\Delta G^{\ddagger}$ at 298 K was found to be 12.8 kcal/mol, while $\Delta H^{\ddagger}$ was found to be 5.1 kcal/mol and $\Delta S^{\ddagger}$ was found to be −26 cal K^{-1} mol^{-1}. The large, negative entropy of activation suggests significant involvement of solvent during bond breaking and suggests a late transition state for bond breaking.

As shown in Figure 3, **2d** undergoes a formal loss of hydrogen peroxide upon standing at 310 K in methanol to give tellurapyrylium dye **1d**. The kinetics of this reaction were also followed spectrophotometrically by monitoring either the rate of disappearance of **2d** at 510 nm or the rate of appearance of **1d** at 810 nm upon heating

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(13) The pK_a is determined spectrophotometrically by a plot of log $[(D_A - D)/(D - D_B)]$ vs pH, where pK_a is the intercept of the y axis, D is the measured optical density at a particular wavelength at a given pH, D_A is the measured optical density of the fully protonated form (at low pH) at the same wavelength, and D_B is the measured optical density of the fully ionized form (at high pH) at the same wavelength.

Table III. Effect of pH on the Rate of Thermal Reduction of 2c at 333 K[a]

pH	10^4k, s^{-1}	pH	10^4k, s^{-1}
1.05	12.3 ± 0.2	7.07	4.04 ± 0.10
3.11	6.27 ± 0.08	7.37	4.66 ± 0.11
4.24	3.93 ± 0.10	8.27	12.3 ± 0.2
5.16	3.45 ± 0.09	9.19	29.2 ± 0.3
5.98	3.10 ± 0.05		

[a] Average of duplicate runs agreeing in value within 4%.

Table IV. Thermal Rates of Reduction and Activation Parameters for 2b–d in PBS at a pH of 7.37 and Thermal Rates of Reduction at a pH of 4.24

compd	pH	*T*, K	10^5k, s^{-1}
2b[a]	7.37	310.0	1.79 ± 0.01
	7.37	323.0	8.29 ± 0.05
	7.37	333.0	20.7 ± 0.3
2c[b]	7.37	310.0	4.42 ± 0.16
	7.37	323.0	20.5 ± 0.3
	7.37	333.0	46.6 ± 1.1
	4.24	310.0	4.00 ± 0.04
	4.24	333.0	39.3 ± 0.2
2d[c]	7.37	310.0	2.24 ± 0.03
	7.37	323.0	9.15 ± 0.02
	7.37	333.0	25.1 ± 0.04
	4.24	310.0	2.38 ± 0.02
	4.24	333.0	25.2 ± 0.1

[a] $\Delta H^\ddagger$ = 21.3 ± 0.6 kcal mol^{-1}, $\Delta S^\ddagger$ = 12 ± 2 cal K^{-1} mol^{-1}, E_a = 21.9 ± 0.6 kcal mol^{-1}, *A* = 24.68 ± 0.25. [b] $\Delta H^\ddagger$ = 20.5 ± 0.9 kcal mol^{-1}, $\Delta S^\ddagger$ = 11 ± 3 cal K^{-1} mol^{-1}, E_a = 21.2 ± 0.9 kcal mol^{-1}, *A* = 24.35 ± 0.42. [c] $\Delta H^\ddagger$ = 20.9 ± 0.1 kcal mol^{-1}, $\Delta S^\ddagger$ = 10.9 ± 0.5 cal K^{-1} mol^{-1}, E_a = 21.4 ± 0.1 kcal mol^{-1}, *A* = 24.26 ± 0.07.

10^{-5} M solutions of **2d** in various combinations of water and methanol.[14] Isosbestic behavior was observed in the conversion of **2d** to **1d** (isosbestic point at 580 nm) such that the rate constants associated with the disappearance of **2d** and the appearance of **1d** are identical. First-order kinetic behavior was observed over at least 3 half-lives. Temperature-dependent first-order rate constants, *k*, for the disappearance of **2d** in aqueous methanol are compiled in Table II and are the average of two or more runs agreeing within 4% of one another.

The activation parameters for the reduction of **2d** to **1d** were determined in 99% aqueous methanol and in 90% aqueous methanol. These values are also listed in Table II. In 99% methanol, a value of 18.5 kcal mol^{-1} was calculated for $\Delta H^\ddagger$ and a value of 15.6 cal K^{-1} mol^{-1} was calculated for $\Delta S^\ddagger$, similar to those determined in methanol-d_4 by ^{1}H NMR spectroscopy. From these values, $\Delta G^\ddagger$ at 298 K is calculated to be 13.9 kcal mol^{-1}. As the percentage of water increases, the value of $\Delta S^\ddagger$ decreases to 11.9 cal K^{-1} mol^{-1} in 90% methanol while the value of $\Delta H^\ddagger$ increases to 18.3 kcal mol^{-1}. The rate of reaction slows at 298 K as the percentage of water increases with $\Delta G_{298}{}^\ddagger$ increasing from 13.9 kcal mol^{-1} in 99% methanol to 14.8 kcal mol^{-1} in 90% methanol.

In 50% aqueous methanol, the rate of reaction decreases further. At 303.0 K, *k* was found to be (2.83 ± 0.02) × 10^{-4} s^{-1} in 50% methanol, (1.27 ± 0.02) × 10^{-3} s^{-1} in 90% methanol, and (5.38 ± 0.25) × 10^{-3} s^{-1} in 99% methanol.

Thermal Reaction of Tellurium(IV) Species 2 in Aqueous Media. In mixtures of methanol and water containing more than 75% water, thermal conversion of **2** to **1** was observed, although other competing reactions were detected. First-order loss of **2** was not observed over the entire reaction. In distilled water, the disappearance of **2** followed a first-order decay over the first 10% of reaction, slowed during the remainder of the first half-life (while not following first-order kinetics), and followed a first-order decay again after the first half-life with a smaller rate constant. This is in marked contrast to the behavior of **2d** in 99% methanol, where first-order behavior was observed over several half-lives.

Effect of pH on the First-Order Rates of Reaction for the Thermal Reduction of Compounds 2. With distilled water as a solvent, attempts to determine first-order rates of reaction for thermal loss of **2** were frustrated by the various equilibria and reaction pathways available to the various species. The use of buffer systems allowed the generation of reproducible kinetics data and the determination of first-order rate constants for the disappearance of **2**.

Table III gives the first-order rates of reaction for the disappearance of **2c** at 333 K as a function of pH. At high pH, **2c** would be fully dissociated and would bear a net negative charge (Scheme II). At buffering pH's above 7.8 (the pK_a of the second acidic proton), the rate of disappearance of **2c** is much greater than the rate of disappearance at a buffering pH of 4–7, where **2c** would be in its zwitterionic form (Scheme II). As the pH is lowered, the rate of disappearance of **2c** increases and the concentration of fully protonated **2c** (Scheme II) also increases. These data suggest that the operative mechanism and rate-determining step in the thermal reduction of **2c** depend upon the pH of the medium.

In order to simplify initial studies of these compounds, the zwitterionic form (net neutral) was first studied in PBS at a pH of 7.37. These conditions were also chosen to mimic the in vivo environment where compounds **2** might be produced via oxidation of tellurapyrylium dyes **1**.

Kinetic Analysis of the Thermal Disappearance of Tellurium(IV) Compounds 2 in PBS. Rates of disappearance of compounds **2b–d** (~3 × 10^{-5} M) were determined at 310.0, 323.0, and 333.0 K in PBS. First-order behavior was observed in all runs for 2–3 half lives ($R^2 \geq$ 0.998), and values of duplicate runs agreed within 4% for each temperature. Values of the first-order rate constant, *k*, are compiled in Table IV. The rates of reaction were also determined at a pH of 4.24 for **2c,d** at 310.0 and 333.0 K. These data are also compiled in Table IV. The rates of disappearance of **2** were nearly identical at both values of pH.

From the values of *k* given in Table IV, values for the Arrhenius parameters as well as the enthalpy and entropy of activation can be determined in PBS. Values of E_a, *A*, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ are nearly identical in all three systems. The average value for $\Delta H^\ddagger$ is ~21 kcal mol^{-1}, while the average value of $\Delta S^\ddagger$ is ~11 cal K^{-1} mol^{-1}. Values for the free energy of activation, $\Delta G^\ddagger$, at 298 K were calculated to be 17.5, 16.9, and 17.4 kcal/mol for **2b–d**, respectively. The rate of reaction of **2d** in PBS is slower than in 90% aqueous methanol and $\Delta G_{298}{}^\ddagger$ (17.4 kcal mol^{-1} in PBS) is correspondingly higher (14.8 kcal mol^{-1} in 90% methanol). The values of the activation parameters are quite similar to the values determined for **2d** in aqueous methanol and suggest that similar rate-determining steps and mechanisms are involved in the thermal reduction of compounds **2** in both solvents.

Mechanistic Considerations. The thermal reduction of compounds **2** to **1** in aqueous methanol appears to follow a markedly different mechanism than thermal halogen-ligand exchange between tellurium atoms. The enthalpy of activation is significantly larger (by 14 kcal mol^{-1}) than that measured for tellurium–halogen exchange, while the entropy of activation is large and positive (~12 kcal/mol).

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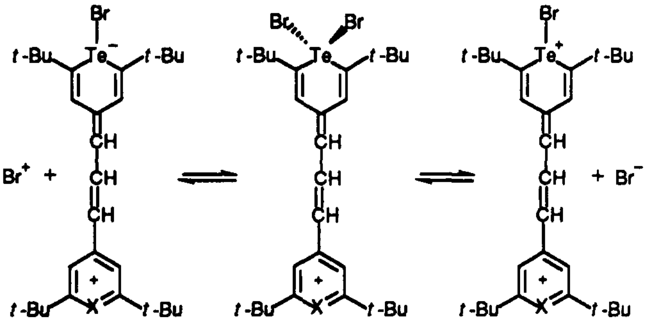
(14) For a preliminary communication of the kinetics data, see: Detty, M. R.; Gibson, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 4086.

Scheme III



These data suggest that solvent reorganization is not as important in the thermal reduction of compound **2d** in the transition state as it is in the transition state for tellurium–halogen exchange and that bond breaking occurs early in the transition state.

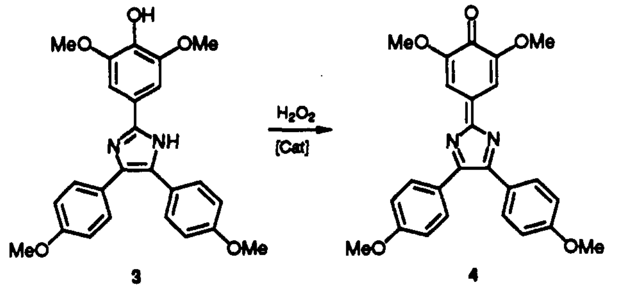
A first-order reaction for tellurium–halogen exchange would necessarily increase the number of charged species as shown in Scheme III. A high-dielectric solvent such as acetonitrile would be expected to facilitate the generation of charged species through solvation. Solvent reorganization would contribute to a large, negative entropy of activation.

In combinations of methanol and water, the solvent sphere should be highly organized around both the negative and positive charges in the zwitterion. Rate-determining loss of negatively charged perhydroxide anion would not increase the number of discrete charges along the reaction coordinate. Similarly, concerted reductive elimination of hydrogen peroxide from protonated **2d** would not increase the number of discrete charges along the reaction coordinate. Consequently, solvent reorganization would play a much smaller role and $\Delta S^{\ddagger}$ might be expected to be positive (reflecting the dissociative process) in either scenario.

Alternatively, homolytic bond cleavage to produce hydroxy and/or hydroperoxy radicals would also be consistent with values of the enthalpy of activation and the entropy of activation determined for thermal reduction of **2d**. Homolytic cleavage would not generate additional charged species requiring solvent reorganization. The homolytic dissociative path would contribute to positive values of $\Delta S^{\ddagger}$.

Product Analysis. Detection of Hydrogen Peroxide in the Thermal Conversion of 2d to 1d. The thermal conversion of **2** to **1** in either aqueous methanol or water requires the formal reductive elimination of hydrogen peroxide from the oxidized dyes **2**. This reaction of a telluroxide equivalent does not have precedent in the chemistry of either selenoxides or sulfoxides.

Leucodye **3** is oxidized to dye **4** with hydrogen peroxide. For useful rates of reaction, horseradish peroxidase (HRP) is required for the net two-electron reduction of peroxide.



3 **4**

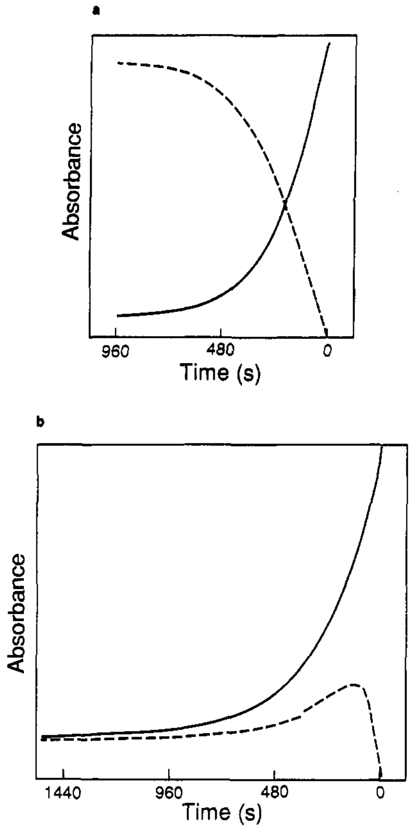


Figure 4. Disappearance of the absorption band of **2d** at 510 nm (solid line) and appearance of the absorption band of **1d** at 810 nm (dotted line) at 333 K as a function of time in (a) 90% methanol and (b) PBS. The absorption intensity is scaled for differences in extinction coefficients.

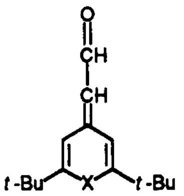
In the presence of HRP (3×10^{-12} M) and 4-hydroxyacetanilide (0.01 M) as an electron-transfer agent, **3** (5×10^{-4} M) is oxidized by hydrogen peroxide (1×10^{-4} M) to give **4** with a final concentration of 1×10^{-4} M at 300 K within 10 min of HRP addition. In the absence of HRP, the pseudo-first-order rate constant for the oxidation of **3** to **4** is less than 10^{-7} s^{-1} at 300 K.

The production of hydrogen peroxide via reductive elimination from **2d** was demonstrated via the oxidation of **3** to **4**. Heating a solution of **2d** (5×10^{-4} M) at 310 K in 90% methanol produced **1d**. The reaction mixture was diluted 5-fold into cold water. The addition of HRP (3×10^{-12} M), 4-hydroxyacetanilide (0.01 M), and leucodye **3** (5×10^{-4} M) to the filtrate gave a reaction mixture that produced **4** with a final concentration of $(9.5 \pm 0.5) \times 10^{-4}$ M at 300 K. These values are nearly identical with the final concentration of **4** produced with 1×10^{-4} M hydrogen peroxide in the presence of HRP. This corresponds roughly to a 95% conversion of **2d** to **1d** and hydrogen peroxide.

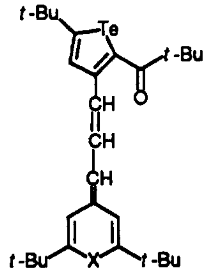
In PBS, similar results were obtained. Following complete disappearance of **2** in PBS (2.0×10^{-4} M), *none* of the reduced dye **1d** can be detected in solution. Leucodye **3** (5×10^{-4} M) and 4-hydroxyacetanilide (0.01 M) were added to the PBS solution following reaction. Upon the addition of 10^{-12} M HRP, leucodye **3** was oxidized to **4**, with a final optical density after 15 min corresponding to a concentration of hydrogen peroxide of $(1.51 \pm 0.10) \times 10^{-4}$ M, which represents roughly a 75% conversion of **2d** to **1d** and hydrogen peroxide.

Detection of Reduced Dyes 1 following Thermal Reaction of 2. The other product produced via reductive elimination of hydrogen peroxide from **2** is the reduced dye **1**. In 90% methanol, thermal first-order loss of **2d** is accompanied by the first-order appearance of **1d** as shown in Figure 4a. The final concentration of **1d** is 95% of the initial concentration of **2d** in Figure 4a. In PBS, thermal first-order loss of **2d** is not accompanied by first-order appearance of **1d**, as shown in Figure 4b. The concentration of **1d** reaches a maximum after approximately 20% loss of **2d** and then decreases with time. These results are consistent with the formation of **1d** from **2d** in both 90% methanol and PBS. However, the rate of hydrolysis of **1d** is much faster in PBS than in 90% methanol (vide infra). Consequently, much lower maximum concentrations of **1d** are observed upon heating **2d** in PBS than in 90% methanol.

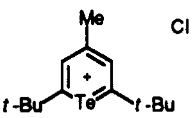
Products of Hydrolysis and Intramolecular Oxidation. In PBS (pH 7.37), thermal reaction of compounds **2** at 333 K produced a number of hexane-soluble products, which were purified by chromatography on silica gel. These products were present in less than 5% combined yield in reactions of **2d** in either 99% or 90% methanol. One product, isolated in 40–64% yield, was identified as (chalcogenapyranylidene)acetaldehyde (**5**) by comparison with authentic samples.[15] A second component of the chromatography, isolated in low yields, contained only aliphatic protons by ^{1}H NMR spectroscopy and appeared to be a mixture of not readily identifiable compounds by field desorption mass spectroscopy (FDMS). This component was not investigated further. A third component, isolated in 25–59% yield as a dark red oil, was determined to be tellurophenes **6**.



5a–d



6a–d



7

X = O (**a**), S (**b**), Se (**c**), Te (**d**)

In PBS at a pH of 7.37, **5d** was isolated in 42% yield and **6d** was isolated in 25% yield following thermolysis of **2d**. Similar results were obtained in the thermolysis of **2c**, where **5c** was isolated in 40% yield and **6c** was isolated in 59% yield. In PBS at pH 7.37, thermolysis of **2b** gave **5b** in 64% isolated yield and **6b** in 34% isolated yield.

Although compound **2a** followed a first-order disappearance upon heating in aqueous solutions, compound **6a**, if produced, was not stable to chromatography on silica gel. Aldehyde **5a** was isolated in 60% yield from thermolysis of **2a** in PBS.

Mass spectral, infrared, and ^{1}H NMR analyses of **6** indicated that **6** was produced by a net loss of a proton and a molecule of water from **2**, that **6** contained a carbonyl group, and that one tellurapyranyl ring and the trimethine bridge remained intact in **6**, respectively. The spectral identification of **6d** serves as an illustrative example. The parent ion of **6d** by FDMS gave a nominal mass of m/z 662 with an isotope pattern consistent with a molecular formula containing two tellurium atoms ($C_{29}H_{42}OTe_2$). The solution infrared spectrum of **6d** displayed stretching frequencies at 1670 and 1622 cm^{-1}, which are consistent with a highly conjugated carbonyl chromophore. The absorption spectrum of **6d** displayed a maximum at 450 nm (ϵ 51 000 cm M^{-1}) consistent with an extended chromophore. The ^{1}H NMR spectrum of **4d** displayed three one-proton singlets, which can be assigned to the two tellurapyranyl ring protons (δ 6.83 and 6.63) and to the tellurophene ring proton (δ 7.76). Four different *tert*-butyl singlets were observed at δ 1.39, 1.29, 1.27, and 1.22. The three protons in the trimethine bridge connecting the two rings appeared as a doublet of doublets (J = 11.7, 15.1 Hz) for one proton at δ 7.09 and two one-proton doublets at δ 6.59 (J = 15.1 Hz) and 6.10 (J = 11.7 Hz).

^{1}H NMR studies of 2-substituted tellurophenes have shown that the 4-proton is observed in the range δ 8.05–7.32.[16] In tellurophenes bearing a carbonyl-containing substituent in the 2-position, the 4-proton is observed in the range δ 8.05–7.87.[16b] The chemical shift of δ 7.76 observed for what is assigned as the tellurophene proton in **6d** is consistent with this range as is the chemical shift of δ 7.75 observed for the 4-proton in both **6b** and **6c**. The chemical shift of the singlet assigned to the 4-proton of the tellurophene is essentially the same in **6b–d**, while the singlets associated with the chalcogenapyranyl protons change much more in chemical shift as the chalcogen atom changes (δ 6.83 and 6.63 for **6d**, δ 6.80 and 6.31 for **6c**, and δ 6.66 and 6.20 for **6b**).

More definitive evidence for the structure of **6c** and **6d** comes from ^{13}C NMR spectral analysis. Signals for 21 different kinds of carbon atoms were detected, including 11 quaternary carbons, 6 methine carbons, and 4 different methyl carbons. Four different *tert*-butyl groups are present, as evidenced by four different quaternary carbons at δ 44.32, 39.65, 39.04, and 38.62 in **6d** and at δ 44.32, 38.61, 38.39, and 37.89 in **6c**. Four different sets of methyl carbons at δ 33.40, 31.04, 30.99, and 27.72 in **6d** and at δ 33.39, 30.22, 30.15, and 27.74 in **6c** complete the *tert*-butyl groups. Quaternary carbons at δ 209.76 and 210.01 can be assigned to the carbonyl carbons of **6d** and **6c**, respectively. These chemical shifts are similar to the chemical shift of δ 194.7 observed for the carbonyl carbon of 2-acetyltellurophene.[16b] The extended conjugation in **6c** and **6d** could account for the 15 ppm downfield shift relative to 2-acetyltellurophene. In comparing the ^{13}C NMR spectra of **6c** and **6d**, the signals associated with the tellurophene rings in the two systems (three quaternary centers and one methine center) would be expected to be quite similar in chemical shift. The quaternary carbons at δ 166.26, 150.01, and 128.77 in **6d** and at δ 166.07, 150.05, and 128.77 in **6c** can be assigned presumably to the quaternary carbons of the tellurophene ring in **6c** and **6d** since these signals change relatively little in the two molecules. The three remaining quaternary signals in the ^{13}C NMR spectrum of **6d** at δ 141.04, 137.99, and 137.63 differ by several ppm in chemical shift from the three remaining quaternary signals in the spectrum of **6c** at δ 149.19, 146.42, and 135.19. These signals can be assigned, presumably, to the quaternary carbons in the chalcogenapyranyl rings. A methine carbon signal at δ 129.63 in **6d** and at δ 129.58 in **6c** can presumably be assigned to the methine carbon of the tellurophene ring of **6d** and **6c**. The remaining methine signals at δ 129.49, 127.50, 127.33, 125.53, and 120.16 in **6d** and at δ 127.30, 125.52, 124.59, 122.35, and 115.25 in **6c** can be assigned to the methine carbons of the chalcogenapyranyl ring and the trimethine bridge of **6d** and **6c**, respectively.

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[15] Wadsworth, D. H.; Detty, M. R.; Murray, B. J.; Weidner, C. H.; Haley, N. F. *J. Org. Chem.* **1984**, *49*, 2676.

[16] (a) Fringuelli, F.; Gronowitz, S.; Hornfeldt, A.-B.; Johnson, I.; Taticchi, A. *Acta Chem. Scand., Ser. B* **1976**, *30*, 605. (b) Fringuelli, F.; Gronowitz, S.; Hornfeldt, A.-B.; Johnson, I.; Taticchi, A. *Acta Chem. Scand., Ser. B* **1974**, *28*, 175.

Table V. Rates of Hydrolysis of Chalcogenapyrylium Dyes 1 in Methanol, Water, and Phosphate Buffers of Varying pH at 310 K

compd	solvent or pH	10^5k, s^{-1} [a]	compd	solvent or pH	10^5k, s^{-1} [a]
1a	99% MeOH	0.15	**1d**	99% MeOH	≤0.05
	water	2.96		90% MeOH	0.07
	7.37	142		50% MeOH	0.51
1b	99% MeOH	≤0.03		water	1.39
	water	0.323		4.24	7.16
	7.37	2.34		7.37	23.9
1c	99% MeOH	≤0.03			
	water	0.97			
	4.24	2.25			
	7.37	7.78			

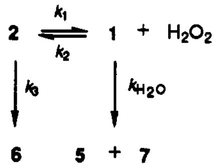
[a] Average of duplicate runs agreeing in value within 4%.

Table VI. Second-Order Rate Constants (k_2) from Pseudo-First-Order Kinetics (k_{obs}) Corrected for Hydrolysis (k_{H_2O}) in PBS at 310 K for the Oxidative Addition of Hydrogen Peroxide to 1

compd	k_{obs},[a] s^{-1}	$k_{obs} - k_{H_2O}$, s^{-1}	$[H_2O_2]$, M	k_2, s^{-1} M^{-1}
1b	$(5.53 \pm 0.10) \times 10^{-4}$	5.30×10^{-4}	10^{-4}	5.30
	$(4.67 \pm 0.03) \times 10^{-3}$	4.65×10^{-3}	10^{-3}	4.65
1c	$(4.46 \pm 0.09) \times 10^{-4}$	3.68×10^{-4}	10^{-4}	3.68
	$(3.14 \pm 0.05) \times 10^{-3}$	3.06×10^{-3}	10^{-3}	3.06
1d	$(7.18 \pm 0.13) \times 10^{-4}$	4.79×10^{-4}	10^{-4}	4.79
	$(4.24 \pm 0.07) \times 10^{-3}$	4.00×10^{-3}	10^{-3}	4.00

[a] Average of duplicate runs agreeing in value within 4%.

Scheme IV



The products formed from heating compounds **2** clearly differ between methanol and water. Formal reductive loss of hydrogen peroxide from **2** would produce **1**, as is observed in methanol. While this process is observed in water, other processes compete. One process leads to the tellurophene products **6**. A second process leads to chalcogenapyranyl acetaldehydes **5** and is presumably due to hydrolysis of the dyes **1**.

Rates of Hydrolysis of Tellurapyrylium Dyes 1 in Aqueous Media. The rates of hydrolysis of the chalcogenapyrylium dyes **1** in 99% methanol, water, and various phosphate buffers are compiled in Table V. The dyes **1** are quite stable to hydrolysis in 99% methanol. However, the rate of hydrolysis increases with increasing water concentration. The dyes are more stable in phosphate buffers of lower pH. The rates of hydrolysis at pH 7.37 in PBS are large enough to account both for the disappearance of **1d** illustrated in Figure 4b and for yields of chalcogenapyranyl acetaldehydes **5** observed during thermal reaction of compounds **2** in PBS.

Preparative hydrolysis of dyes **1** in PBS at 333 K gave 2,6-di-*tert*-butyl-4-methyltellurapyrylium chloride (**7**) in 50–60% isolated yield and aldehydes **5** in greater than 90% yield. The tellurophenes **6** were stable under conditions that gave complete hydrolysis of tellurapyrylium dyes **1**.

Oxidation of Tellurapyrylium Dyes 1 with Hydrogen Peroxide in 99% Aqueous Methanol and in Phosphate-Buffered Saline. In postulating mechanisms for the thermal reduction of compounds **2** to tellurapyrylium dyes **1** and hydrogen peroxide, the kinetics of the oxidation of **1** to **2** with hydrogen peroxide must be considered. Since the addition of hydrogen peroxide to tellurapyrylium dyes **1** represents a preparative route to compounds **2**, thermal reductions postulating the reductive elimination of hydrogen peroxide or hydroperoxy anion must account for the reverse reaction.

Second-order rate constants for the addition of hydrogen peroxide to tellurapyrylium dyes **1** can be calculated under pseudo-first-order conditions. In 99% methanol at 310 K, a 10^{-5} M solution of **1d** is oxidized by 10^{-3} M hydrogen peroxide with a pseudo-first-order rate constant of $(1.29 \pm 0.1) \times 10^{-5}$ s^{-1}. At 10^{-4} M hydrogen peroxide, a 10^{-5} M solution of **1d** was oxidized with a pseudo-first-order rate constant of $(1.32 \pm 0.02) \times 10^{-6}$ s^{-1}. From the hydrogen peroxide concentrations employed, the second-order rate constant, k_2, for the addition of hydrogen peroxide to **1d** in 99% aqueous methanol is calculated to be approximately 1.3×10^{-2} s^{-1} M^{-1}.

In distilled water, a 10^{-5} M solution of **1d** is oxidized by 10^{-3} M hydrogen peroxide at 310 K with a pseudo-first-order rate constant of $(2.02 \pm 0.02) \times 10^{-3}$ s^{-1}. At 10^{-4} M hydrogen peroxide, a 10^{-5} M solution of **1d** is oxidized at 310 K with a pseudo-first-order rate constant of $(1.98 \pm 0.03) \times 10^{-4}$ s^{-1}. From the concentrations of hydrogen peroxide employed, the second-order rate constant for the addition of hydrogen peroxide to **1d** at 310 K is calculated to be 2.00 M^{-1} s^{-1}.

In PBS, attempts to measure second-order rate constants under pseudo-first-order conditions were complicated by competing hydrolysis of the tellurapyrylium dyes **1** (Table V). As shown in Table VI, the observed loss of dye **1** in the presence of hydrogen peroxide (k_{obs}) can be corrected for the dye lost due to hydrolysis in PBS at 310 K (k_{H_2O}). From this treatment, k_2 for **1d** was found to be 4.4 s^{-1} M^{-1}, k_2 for **1c** was found to be 3.4 s^{-1} M^{-1}, and k_2 for **1b** was found to be 5.0 s^{-1} M^{-1}. Interestingly, the second-order rate constant for the addition of hydrogen peroxide to **1d** was found to be hundreds of times larger in water and PBS than in 99% aqueous methanol. This difference in rate may reflect different oxidants in the two solvents with hydrogen peroxide as the oxidant in 99% aqueous methanol and hydroperoxy anion as the oxidant in water or PBS.

Equilibria Involving Hydrogen Peroxide, Tellurapyrylium Dye 1d, and Oxidized Dye 2d. The various reactions of **1**, **2**, and hydrogen peroxide are summarized in Scheme IV. Under ideal conditions, only the equilibrium between **2** and equimolar quantities of **1** and hydrogen peroxide would be established upon heating solutions of **2**. The equilibrium constant for this reaction could be easily calculated from values of k_1 and k_2. However, hydrolysis of the reduced dye **1** removes **1** (with a rate constant of k_{H_2O}) from the equilibrium and reaction of the oxidized species **2** to give other products (with a rate constant of k_3) removes **2** from the equilibrium. In 99% methanol, both k_{H_2O} and k_3 are small relative to k_1 and k_2 such that good values for both k_1 and k_2 can be measured directly and k_3 and k_{H_2O} can be ignored. In PBS, k_{H_2O} is large relative to k_1. Consequently, **1** is being removed from the equilibrium nearly as fast as it is being formed. This allows k_1 to be measured directly and k_2 to be measured by allowing for k_{H_2O}. In PBS, k_3 cannot be ignored, since products **6** are produced in 25–59% isolated yields.

In distilled water, the value of the rate constant k_3 was calculated to be 5.17×10^{-6} s^{-1} for **2d** at 310 K from studies where equilibrium concentrations of **1**, **2**, and hydrogen peroxide were approached. As equilibrium is approached, the disappearance of **2** will reflect the rate of reaction of **2** to give other products. With a starting concentration of **2d** of 4.0×10^{-5} M in distilled water, equilibrium con-

Table VII. Effect of Added Peroxide on First-Order Rates of Disappearance of 2d in PBS

[**2d**],[a] M	[H_2O_2], M	$10^5 k_{obs}$, s^{-1} [b]
1×10^{-5}	0.0	2.24 ± 0.03
1×10^{-5}	1×10^{-5}	2.02 ± 0.05
1×10^{-5}	1×10^{-4}	2.30 ± 0.07
1×10^{-5}	1×10^{-3}	5.33 ± 0.28
3×10^{-5}	0.0	2.24 ± 0.03
3×10^{-5}	1×10^{-5}	2.07 ± 0.06
3×10^{-5}	1×10^{-4}	2.89 ± 0.14

[a] Initial concentration. [b] Average of duplicate runs agreeing in value within 4%.

centrations of 2.8×10^{-5} M for **2d** and 1.2×10^{-5} M for both **1d** and hydrogen peroxide can be calculated at 310 K on the basis of k_1 (1.01×10^{-5} s^{-1}) and k_2 (2.00 M^{-1} s^{-1}). When hydrogen peroxide was added to a concentration of 1.0×10^{-4} M with **2** at 4.0×10^{-5} M, equilibrium concentrations of 1.02×10^{-4} M in hydrogen peroxide, 1.8×10^{-6} M in **1**, and 3.8×10^{-5} M in **2** at 310 K were calculated. In a system initially at 2.0×10^{-5} M in both **2** and hydrogen peroxide, equilibrium concentrations of 2.35×10^{-5} M in hydrogen peroxide, 3.5×10^{-6} M in **1**, and 1.65×10^{-5} M in **2** can be calculated. In all three systems at 310 K, k_1 was observed to be $(1.01 \pm 0.02) \times 10^{-5}$ s^{-1} over the first 10% of reaction, slowing to $(5.17 \pm 0.03) \times 10^{-6}$ s^{-1} after the first half-life. The latter value is the observed value for k_3, which is presumably a first-order rate constant since varying concentrations of **1** and hydrogen peroxide have little effect on k_3.

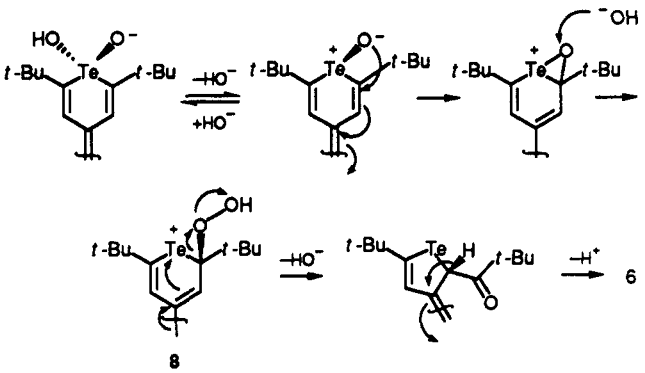
Effect of Added Hydrogen Peroxide on the Thermal Disappearance of 2d in PBS. In order to determine the first-order rate constant for reductive elimination of hydrogen peroxide from **2d** as well as the rate constant for formation of **6d** in PBS, the effect of added hydrogen peroxide on the (presumed) first-order rate constant for disappearance of **2d** was explored. If hydrogen peroxide were in large excess, the equilibrium would be driven toward **2d**. At a high peroxide concentration (1×10^{-3} M) relative to a concentration of 1×10^{-5} M in **2d**, the equilibrium concentration of **1d** would be lowered and would be less than 1×10^{-7} M. Equilibrium concentrations of **2d** and **1d** should be approached within a few percent of reaction. Ideally, the rate of disappearance of **2d** under these conditions should reflect the rate of formation of **6d**. Rate constants for the disappearance of **2d** in PBS in the presence of varying concentrations of hydrogen peroxide are compiled in Table VII.

From the data in Table VII, added hydrogen peroxide has little effect on the rate constant for disappearance of **2d**. At 10^{-5} M hydrogen peroxide, some lowering of k_{obs} is noted. At higher concentrations of added hydrogen peroxide, k_{obs} increases but this increase is consistent with a second-order reaction between hydrogen peroxide and **2d** with a second-order rate constant of $\sim 3 \times 10^{-2}$ s^{-1} M^{-1}. From these data and product distribution data, the rate constant for formation of **6d** can be estimated to be between 1×10^{-5} and 2×10^{-5} s^{-1}.

Mechanism of Formation of Tellurophenes 6. The formation of tellurophenes **6** from dihydroxytelluranes **2** requires the reduction of a tellurium(IV) center to a tellurium(II) center, contraction of a six-membered ring to a five-membered ring, and oxidation of a carbon center. The conversion of **2** to **6** also involves the net loss of a molecule of water and a proton from **2**.

As shown in Scheme V, postulation of **8** as an intermediate in the conversion of **2** to **6** would allow a consistent mechanism for the ring-contraction step, the oxidation of the carbon adjacent to tellurophene, and the loss of a proton to be proposed. The formation of **8** might arise from the reductive elimination of hydrogen peroxide from **2** to give **1** followed by addition of hydroperoxy anion to the 2-position of the dye. If the readdition of hydroperoxy anion to the reduced dye **1** were important to the overall conversion of **2** to **6**, then the concentration of peroxide in the reaction mixture would be expected to influence the rate of formation of **6** from **2**. This is not observed in either water or PBS, where added peroxide has little effect on the observed rate of formation of **6** from **2**. Furthermore, the oxidative addition of hydrogen peroxide to tellurapyrylium dyes **1** gives only oxidized dyes **2** at low conversions of **1** to **2** with peroxide in PBS. Tellurophene **6** is not detected.

Scheme V



Alternatively, an intermediate such as **8** could be formed via intramolecular oxidation of the carbon center adjacent to tellurium. If the zwitterionic form of **2** were in equilibrium with the telluroxide form (via addition or loss of hydroxide), then intramolecular oxidation of carbon followed by ring opening with hydroxide would give **8** as shown in Scheme V. If the intramolecular oxidation of carbon were the rate-determining step, then the rate constant for formation of **6** would be fairly constant over the pH range where **2** is zwitterionic. Product yields for the formation of **6** were nearly identical in buffers of pH 4.24 and 7.37, suggesting similar rate constants for the formation of **6**.

Summary and Conclusions

The dihydroxytelluranes **2** are special examples of hydrated telluroxides in which the molecules bear a formal positive charge. The positive charge affects the chemistry of dihydroxytelluranes **2** by increasing the acidity of the hydroxyl protons such that compounds **2** exist in zwitterionic form in aqueous solution at pH 4.27–7.37 and decreasing the free energy of activation for the reductive elimination of hydrogen peroxide (or hydroperoxy anion) in various combinations of methanol and water to give reduced dyes **1**. The reductive elimination of hydrogen peroxide is not competitive with other reaction pathways in selenoxides and sulfoxides in aqueous media and is characterized in chalcogen(IV) oxides only with dihydroxytelluranes **2**.

The oxidation of carbon via oxygen atom transfer from a sulfoxide or selenoxide has been documented with both intermolecular and intramolecular examples.[1-3] Similar reactions of telluroxides or dihydroxytelluranes have not been previously described. The formation of **6** from rearrangement of **2** is the first example of selenoxide-like (or sulfoxide-like) oxygen atom transfer from tellurium to carbon in an organotellurium compound.

From the similarity of values of ΔH^{*} and ΔS^{*} calculated from the temperature-dependent rate constants for the disappearance of **2**, the transition states leading to products appear to be similar in 99% methanol, 90% methanol, distilled water, and phosphate buffers of pH 4.24 and 7.37. Values of ΔG^* increase with increasing water concentration. Other examples of neutral and positively charged dihydroxytelluranes are being studied to understand better those parameters influencing the rate of reductive elimination of hydrogen peroxide from tellurium(IV).

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a General Electric QE 300 instrument. Microanalyses were obtained with a Perkin-Elmer C, H, and N analyzer. Infrared spectra were recorded on a Perkin-Elmer 1760 infrared Fourier transform spectrometer. UV–visible–near-IR spectra were recorded on either a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer or on a Perkin-Elmer 330 spectrophotometer equipped with a digital temperature controller. Water was purified by passing distilled water through a Barnstead NANOpure water purification system. Methanol was distilled from magnesium turnings (1.5 g/300 mL) and iodine (0.5 g/300 mL). Dyes 1 were prepared by the literature procedure.[12a]

Preparation of 10^{-3} M Stock Solutions of 2b. Dye **1b** (0.12 g, 0.20 mmol) was dissolved in 20 mL of methanol. The resulting solution was added dropwise to 200 mL of phosphate-buffered saline (PBS) in a Pyrex beaker with magnetic stirring. During the addition (~15 min), the beaker was irradiated with a GE sunlamp and was cooled in an ice–water bath. The reaction mixture was extracted with dichloromethane (3 × 25 mL) to remove unreacted **1b**. The aqueous solution contained 9.3×10^{-4} M **2b** as measured spectrophotometrically: λ_{max} 480 nm (log ϵ 4.72).

Preparation of 10^{-3} M Stock Solutions of 2c. Dye **1c** (0.13 g, 0.20 mmol) in 20 mL of methanol was added to 180 mL of PBS with irradiation as described for the preparation of **2b**. The resulting stock solution of **2c** contained 8.7×10^{-4} M **2c** as measured spectrophotometrically: λ_{max} 502 nm (log ϵ 4.74).

Preparation of 10^{-3} M Stock Solutions of 2d. Dye **1d** (0.30 g, 0.44 mmol) in 50 mL of methanol was added dropwise to 350 mL of PBS with irradiation as described for the preparation of **2b**. The resulting stock solution of **2d** contained 9.9×10^{-4} M **2d** as measured spectrophotometrically: λ_{max} 510 nm (log ϵ 4.75).

Hydrogen Peroxide Oxidation of 1c and 1d. Hydrogen peroxide (150 μL of a 30% solution, 1.5 mmol) was added via syringe to a solution of 1 mmol of **1b**, **1c**, or **1d** (as the PF_6 salts)[7a] in 25 mL of methanol cooled to 0 °C. The resulting solution was stirred for 10 min at 0 °C and was then concentrated in vacuo at 0 °C. The maroon powder was collected by filtration, washed with ether, and dried to give **2b–d** in 72%, 75%, and 82% yields, respectively. These compounds decomposed rapidly above 75 °C during attempts to obtain melting points.

2b: ^{1}H NMR (MeOH-d_4) δ 8.65 (s, 2 H), 8.59 (d × d, 1 H, J = 12, 15 Hz), 7.28 (d, 1 H, J = 15 Hz), 6.95 (s, 1 H), 6.93 (d, 1 H, J = 12 Hz), 6.39 (s, 1 H), 1.67 (s, 18 H), 1.52 (s, 9 H), 1.48 (s, 9 H). Anal. Calcd for $C_{29}H_{45}O_2STePF_6$: C, 47.64; H, 6.20. Found: C, 47.31; H, 6.42.

2c: ^{1}H NMR (MeOH-d_4) δ 8.81 (d × d, 1 H, J = 12.0, 15.1 Hz), 8.69 (s, 2 H), 7.36 (s, 1 H), 7.33 (d, 1 H, J = 15.1 Hz), 7.07 (d, 1 H, J = 12.0 Hz), 6.74 (s, 1 H), 1.65 (s, 18 H), 1.52 (s, 9 H), 1.48 (s, 9 H). Anal. Calcd for $C_{29}H_{45}O_2SeTePF_6$: C, 45.10; H, 5.87. Found: C, 45.23; H, 5.45.

2d: ^{1}H NMR (MeOH-d_4) δ 8.88 (d × d, 1 H, J = 12.0, 14.8 Hz), 8.68 (s, 2 H), 7.33 (s, 1 H), 7.28 (d, 1 H, J = 14.8 Hz), 7.00 (d, 1 H, J = 12.0 Hz), 6.72 (s, 1 H), 1.68 (s, 18 H), 1.52 (s, 9 H), 1.47 (s, 9 H). Anal. Calcd for $C_{29}H_{45}O_2Te_2PF_6$: C, 42.95; H, 5.59. Found: C, 42.60; H, 5.61.

Preparative Thermolysis of 2d in PBS. The stock solution of **2d** in PBS (9.9×10^{-4} M, 220 mL, 0.22 mmol) was heated at 80 °C for 2 h. The reaction mixture was cooled to ambient temperature, and the products were extracted with hexane (3 × 100 mL). The combined hexane extracts were dried over sodium sulfate and concentrated. The residue was purified by chromatography on silica gel with 12% ethyl acetate in hexane as eluent. One component from the chromatography (R_f 0.6) was isolated in 0.037 g (25%) yield as a dark red oil identified as **6d**. A second product (R_f 0.25) was isolated in 0.030 g (42%) yield as a dark red oil identified as **5d**.

5d: ^{1}H NMR (CDCl$_3$) δ 10.10 (d, 1 H, J = 6 Hz), 7.98 (s, 1 H), 6.65 (s, 1 H), 5.70 (d, 1 H, J = 6 Hz), 1.40 (s, 9 H), 1.33 (s, 9 H); IR (CHCl$_3$) 1670 cm^{-1}; FDMS m/z 348 ($C_{15}H_{22}O^{130}Te$).

6d: ^{1}H NMR (CDCl$_3$) δ 7.76 (s, 1 H), 7.09 (d × d, 1 H, J = 11.7, 15.1 Hz), 6.83 (s, 1 H), 6.59 (d, 1 H, J = 15.1 Hz), 6.63 (s, 1 H), 6.10 (d, 1 H, J = 11.7 Hz), 1.39 (s, 9 H), 1.29 (s, 9 H), 1.27 (s, 9 H), 1.22 (s, 9 H); ^{13}C NMR (CDCl$_3$) δ 209.76, 166.26, 150.01, 141.04, 137.99, 137.63, 129.63 (CH), 129.49 (CH), 128.77, 127.50 (CH), 127.33 (CH), 125.53 (CH), 120.16 (CH), 44.32, 39.65, 39.04, 38.62, 33.40 (CH$_3$), 31.04 (CH$_3$), 30.99 (CH$_3$), 27.72 (CH$_3$); IR (hexane) 1665, 1622 cm^{-1}; FDMS m/z 666 ($C_{29}H_{42}O^{130}Te_2$). Anal. Calcd for $C_{29}H_{42}OTe_2$: C, 52.62; H, 6.40; Te, 38.56. Found: C, 52.63; H, 6.34; Te, 38.10.

Preparative Thermolysis of 2c in PBS. The stock solution of **2c** in PBS (8.7×10^{-4} M, 175 mL, 0.16 mmol) was heated at 80 °C for 2 h. The reaction mixture was cooled to ambient temperature, and the products were extracted with hexane (3 × 100 mL). The combined hexane extracts were dried over sodium sulfate and concentrated. The residue was purified by chromatography on silica gel with 12% ethyl acetate in hexane as eluent. One component from the chromatography (R_f 0.6) was isolated in 0.057 g (59%) yield as a dark red oil identified as **6c**. A second product (R_f 0.25) was isolated in 0.019 g (40%) yield as a dark red oil identified as **5c**.

5c: ^{1}H NMR (CDCl$_3$) δ 10.05 (d, 1 H, J = 6 Hz), 8.00 (s, 1 H), 6.61 (s, 1 H), 5.70 (d, 1 H, J = 6 Hz), 1.40 (s, 9 H), 1.33 (s, 9 H); IR (CHCl$_3$) 1665 cm^{-1}; FDMS m/z 298 ($C_{15}H_{22}O^{80}Se$).

6c: ^{1}H NMR (CDCl$_3$) δ 7.75 (s, 1 H), 7.06 (d × d, 1 H, J = 11.7, 15.1 Hz), 6.80 (s, 1 H), 6.54 (d, 1 H, J = 15.1 Hz), 6.31 (s, 1 H), 5.91 (d, 1 H, J = 11.7 Hz), 1.38 (s, 9 H), 1.26 (s, 18 H), 1.24 (s, 9 H); ^{13}C NMR (CDCl$_3$) δ 210.01, 166.07, 150.05, 149.19, 146.42, 135.19, 129.58 (CH), 127.30 (CH), 126.69, 125.52 (CH), 124.59 (CH), 122.35 (CH), 115.25 (CH), 44.32, 38.61, 38.39, 37.89, 33.39 (CH$_3$), 30.22 (CH$_3$), 30.15 (CH$_3$), 27.74 (CH$_3$); IR (hexane) 1670, 1625 cm^{-1}; FDMS m/z 616 ($C_{29}H_{42}O^{80}Se^{130}Te$).

Preparative Thermolysis of 2b in PBS. The stock solution of **2b** in PBS (9.3×10^{-4} M, 330 mL, 0.30 mmol) was heated at 80 °C for 2 h. The reaction mixture was cooled to ambient temperature, and the products were extracted with hexane (3 × 100 mL). The combined hexane extracts were dried over sodium sulfate and concentrated. The residue was purified by chromatography on silica gel with 12% ethyl acetate in hexane as eluent. One component from the chromatography (R_f 0.6) was isolated in 0.058 g (34%) yield as a dark red oil identified as **6b**. A second product (R_f 0.25) was isolated in 0.048 g (64%) yield as a dark red oil identified as **5b**.

5b: ^{1}H NMR (CDCl$_3$) δ 10.20 (d, 1 H, J = 6 Hz), 8.00 (s, 1 H), 6.65 (s, 1 H), 5.70 (d, 1 H, J = 6 Hz), 1.32 (s, 9 H), 1.30 (s, 9 H); IR (CHCl$_3$) 1665 cm^{-1}; FDMS m/z 250 ($C_{15}H_{22}OS$).

6b: ^{1}H NMR (CDCl$_3$) δ 7.75 (s, 1 H), 7.01 (d × d, 1 H, J = 11.7, 15.1 Hz), 6.66 (s, 1 H), 6.46 (d, 1 H, J = 15.1 Hz), 6.20 (s, 1 H), 5.70 (d, 1 H, J = 11.7 Hz), 1.37 (s, 9 H), 1.27 (s, 18 H), 1.25 (s, 9 H), 1.22 (s, 9 H); IR (hexane) 1705, 1625 cm^{-1}; FDMS m/z 568 ($C_{29}H_{42}OS^{130}Te$).

Preparative Thermolysis of 2a in PBS. Dye **1a** (0.114 g, 0.20 mmol) was dissolved in 10 mL of methanol. The resulting solution was added dropwise to 200 mL of a 10^{-3} M solution of hydrogen peroxide in PBS cooled to 10 °C. After addition was complete, the reaction mixture was stirred for 20 min. The aqueous solution was extracted with dichloromethane (3 × 25 mL). The aqueous solution was then heated at 80 °C for 2 h. The reaction mixture was cooled to ambient temperature, and the products were extracted with hexane (3 × 100 mL). The combined hexane extracts were dried over sodium sulfate and concentrated. The residue was purified by chromatography on silica gel with 12% ethyl acetate in hexane as eluent. One component from the chromatography (R_f 0.15) was isolated in 0.028 g (60%) yield and was identified as aldehyde **5a**: ^{1}H NMR (CDCl$_3$) δ 9.78 (d, 1 H, J = 6 Hz), 6.51 (s, 1 H), 6.49 (s, 1 H), 5.33 (d, 1 H, J = 6 Hz), 1.32 (s, 9 H), 1.30 (s, 9 H); IR (CH$_2$Cl$_2$) 1670 cm^{-1}; FDMS m/z 234 ($C_{29}H_{42}O_2$).

Preparation of Samples for Kinetics Runs in 99% Methanol. A stock solution of (2–3) × 10^{-3} M **1d** in methanol was prepared. A 35-μL aliquot of this solution and a 35-μL aliquot of water were placed in a quartz cuvette and were irradiated with a GE sunlamp through Pyrex for 3.0 min. The resulting solution of **2d** was diluted with 3.43 mL of methanol (distilled from magnesium turnings and iodine) brought to constant temperature in the spectrophotometer, and the loss of the chromophore associated with **2** was measured as a function of time. An infinity point was determined at >10 half-lives.

Preparation of Samples for Kinetics Runs in 90% Methanol. A stock solution of $(2-3) \times 10^{-3}$ M **1d** in methanol was prepared. A 35-μL aliquot of this solution and a 350-μL aliquot of water were placed in a quartz cuvette and were irradiated with a GE sunlamp through Pyrex for 3.0 min. The resulting solution of **2d** was diluted with 3.115 mL of methanol (distilled from magnesium turnings and iodine). The resulting solution was brought to constant temperature in the spectrophotometer, and the loss of the chromophore associated with **2** was measured as a function of time. An infinity point was determined at >10 half-lives.

Preparation of Samples for Kinetics Runs in 50% Methanol. A stock solution of $(2-3) \times 10^{-3}$ M **1d** in methanol was prepared. A 35-μL aliquot of this solution and a 35-μL aliquot of water were placed in a quartz cuvette and were irradiated with a GE sunlamp through Pyrex for 3.0 min. The resulting solution of **2d** was diluted with 3.43 mL of 50% methanol. The methanol was distilled from magnesium turnings and iodine. The resulting solution was brought to constant temperature in the spectrophotometer, and the loss of the chromophore associated with **2** was measured as a function of time. An infinity point was determined at >10 half-lives.

Preparation of Samples for Kinetics Runs in PBS. A stock solution of $(2-3) \times 10^{-3}$ M **1** in methanol was prepared. A 35-μL aliquot of this solution and a 35-μL aliquot of water were placed in a quartz cuvette and were irradiated with a GE sunlamp through Pyrex for 3.0 min. The resulting solution of **2** was diluted with 3.43 mL of PBS. The resulting solution was brought to constant temperature in the spectrophotometer, and the rate of loss of the chromophore associated with **2** was measured as a function of time. An infinity point was determined at >10 half-lives.

Hydrolysis Rates of Tellurapyrylium Dyes 1 in Water or Phosphate Buffers of Varying pH. Stock solutions of tellurapyrylium dyes **1** (1×10^{-3} M) in methanol were prepared. A 35-μL aliquot of this solution was diluted with buffer (or water) to 3.50 mL in a 1-cm quartz cuvette. The cuvette was brought to constant temperature in the spectrophotometer, and the rate of loss of the chromophore associated with **1** was measured as a function of time. An infinity point was measured at >10 half-lives. Duplicate runs agreeing within 4% were made for each compound.

Preparative Studies of Hydrolysis Products of Tellurapyrylium Dyes 1 in PBS at 333 K. Tellurapyrylium dye **1** (0.10 mmol) was dissolved in 2 mL of methanol. The resulting solution was added dropwise to 200 mL of PBS in a foil-covered flask with stirring. The resulting solution was heated at 333 K for 2 h. The reaction mixture was cooled to ambient temperature. Aldehyde **5** was extracted with ether (3 × 25 mL). The combined organic extracts were dried over sodium sulfate and concentrated in vacuo. The residue was purified via chromatography on silica gel eluted with 5% ethyl acetate in dichloromethane to give the aldehydes **5** in greater than 90% isolated yield. Tellurapyrylium salt **7** was recovered from the reaction mixture via continuous extraction with dichloromethane. The dichloromethane extract was dried over sodium sulfate and concentrated. The residue was crystallized by the addition of 20 mL of ether. The product yield of **7** was 50–60%: mp 138–142 °C; ^{1}H NMR ($CDCl_3$) δ 8.05 (s, 2 H), 2.44 (s, 3 H), 1.67 (s, 18 H).

Second-Order Rate Constants for the Oxidative Addition of Hydrogen Peroxide to Tellurapyrylium Dyes 1 in PBS. Stock solutions of 1×10^{-3} M hydrogen peroxide in PBS and 1×10^{-4} M hydrogen peroxide in PBS were prepared by diluting 107 and 11 μL of 30% hydrogen peroxide, respectively, in 1.0 L of PBS. A 35-μL aliquot of one of the 1×10^{-3} M stock solutions of dyes **1** was added to 3.50 mL of peroxide in PBS in a 1-cm quartz cuvette. The cuvette was brought to constant temperature in the spectrophotometer, and the rate of disappearance of **1** was monitored as a function of time. The observed pseudo-first-order rate constant was corrected for the rate of hydrolysis of the dyes **1** in PBS. Duplicate runs agreeing within 4% were made for each compound.

Kinetics Runs Showing the Effect of Added Peroxide on the Rate of Disappearance of Oxidized Tellurapyrylium Dye 2d in PBS. A 35-μL aliquot of the 1×10^{-3} M stock solution of **1d** in methanol and 35 μL of water were irradiated for 3 min with a GE sunlamp in a 1-cm quartz cuvette. The resulting solution of **2d** was diluted with 3.43 mL of the 1×10^{-3} M stock solution of peroxide in PBS, 3.43 mL of the 1×10^{-4} M stock solution of peroxide in PBS, or 35 μL of the 1×10^{-3} M stock solution of peroxide in PBS and 3.40 mL of PBS to generate 1×10^{-5} M solutions of **2d** in PBS containing 10^{-3}, 10^{-4}, or 10^{-5} M peroxide, respectively. Similar dilutions with irradiated 105-μL aliquots of the 1×10^{-3} M stock solution of **1d** and 35 μL of water gave 3×10^{-5} M solutions of **2d** in PBS containing 10^{-3}, 10^{-4}, or 10^{-5} M peroxide. These solutions were brought to constant temperature in the spectrophotometer, and the rate of disappearance of the chromophore associated with **2d** was monitored at 510 nm as a function of time.

Second-Order Rate Constant for the Addition of Hydrogen Peroxide to 1d in 99% Methanol. A stock solution of hydrogen peroxide in distilled water was prepared by diluting 1.07 mL of 30% hydrogen peroxide to 100.0 mL with distilled water. a 35-μL aliquot of this solution was added to 3.43 mL of methanol in a 1-cm quartz cuvette. A 35-μL aliquot of the 1×10^{-3} M stock solution of **1d** in methanol was added. The resulting solution was brought to constant temperature in a spectrophotometer. The rate of disappearance of the chromophore associated with **1d** was monitored at 815 nm as a function of time.

Registry No. **1a**·PF_6^-, 131903-93-0; **1b**·PF_6^-, 131691-49-1; **1c**·PF_6^-, 124620-12-8; **1d**·PF_6^-, 126876-77-5; **2a**·PF_6^-, 126876-90-2; **2b**·PF_6^-, 126876-92-4; **2c**·PF_6^-, 126876-93-5; **2d**·PF_6^-, 126876-94-6; **5a**, 41857-75-4; **5b**, 131903-97-4; **5c**, 103817-96-5; **5d**, 103817-95-4; **6b**, 131903-96-3; **6c**, 131903-95-2; **6d**, 131903-94-1; **7**, 131903-98-5; H_2O_2, 7722-84-1.