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Reductive Elimination of Chlorine from Dichlorotellurium(IV) Compounds. Kinetic Studies in Tetrachloroethane and Acetonitrile

Michael R. Detty* and Timothy M. Frade

Chemical Technology Laboratory, Office Imaging Research and Technical Development, Eastman Kodak Company, Rochester, New York 14650

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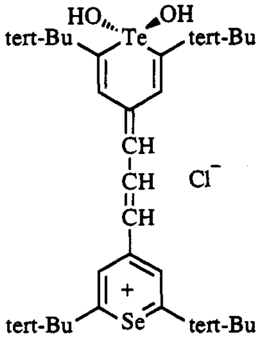
The oxidative addition of chlorine to tellurapyrylium dyes gives dichlorotellurium(IV) dyes that absorb at shorter wavelengths than the corresponding tellurapyrylium dyes. Selenapyrylium dyes do not undergo this reaction but are chlorinated in the hydrocarbon π-framework. In dilute solution (10^{-5} M), the dichlorotellurium(IV) compounds undergo reductive elimination via a first-order process in both tetrachloroethane and acetonitrile to regenerate the tellurapyrylium dye with values of E_a in the range 18.5–24.1 kcal mol^{-1}, ln A in the range 19.9–26.9, $\Delta H^{\ddagger}$ in the range 16.8–23.4 kcal mol^{-1}, and $\Delta S^{\ddagger}$ in the range −1 to +16 cal mol^{-1} K^{-1}. The differences in rate constants between tetrachloroethane and acetonitrile are small, suggesting intermediates or transition states that develop little charge along the reaction coordinate. The chloride ion is found to be a catalyst in these reactions with values of k_{cat} in the range (7.6–22.6) $\times 10^{1}$ mol^{-1} s^{-1} in tetrachloroethane and 7.62×10^{2} mol^{-1} s^{-1} in acetonitrile. The regeneration of aromaticity is thought to be the driving force to accelerate reductive elimination from tellurium(IV) derivatives of cationic dyes relative to neutral tellurium(IV) compounds.

Introduction

The use of a tellurium(IV)–tellurium(II) shuttle in organic redox reactions is appearing more frequently in organic and organometallic chemistry. Arene tellurinic anhydrides have been employed as mild oxidants for a variety of organic substrates including thiols, phosphines, and hydroquinones.[1] Telluroxides have been employed as two-electron oxidants in similar reactions,[2] as have dihalotellurium(IV) derivatives.[3] A catalytic scheme using 1,2-dibromotetrachloroethane as a brominating oxidant of tellurium(II) has been developed in which telluroxides produced in situ are the working oxidant.[4] Dihydroxytellurium(IV) intermediates have been the working oxidant for various oxidations with either hydrogen peroxide or singlet oxygen.[5] Tribromotellurium(IV) species (with an odd number of ligands to tellurium) have functioned as mild oxidants for thiols and selenols.[3b,6]

The mechanistic details of both the oxidative addition to tellurium(II) species to give tellurium(IV) species and the reductive elimination from tellurium(IV) species to give tellurium(II) species have been little explored. The kinetics of the reductive elimination of hydrogen peroxide from dihydroxytellurium(IV) compound 1 in phosphate buffered saline (pH 7.4) show that the reductive elimination is first order with respect to the tellurium(IV) compound and that activation barriers are approximately 21 kcal mol^{-1} for $\Delta H^{\ddagger}$ and approximately 11 cal mol^{-1} K^{-1} for $\Delta S^{\ddagger}$ for the reductive elimination of hydrogen peroxide.[7]



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Both the oxidative-addition and reductive-elimination pathways appear to be two-electron processes. As summarized in Scheme I, either electrochemical (X = halide, OH) or thermal (X = OH) reduction of the tellurium(IV) species gives no detectable tellurium(III) intermediates.[8] Similarly, electrochemical oxidation of halide in the presence of the tellurium(II) compound regenerates the tellurium(IV) compound.

Halogen exchange reactions between tellurium(IV) and tellurium(II) are formally reductive-elimination and oxidative-addition reactions, respectively. Nefedov and coworkers employed isotopic labeling to follow halogen exchange between diphenyltellurium dihalides and di-

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[1] Hu, A. X.; Aso, Y.; Otsubo, T.; Ogura, F. *Phosphorus Sulfur* **1988**, *38*, 177–189. Hu, N. X.; Aso, Y.; Otsubo, T.; Ogura, F. *Tetrahedron Lett.* **1986**, *27*, 6099–7102. Barton, D. H. R.; Finet, J.; Thomas, M. *Tetrahedron* **1986**, *42*, 2319.

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[3] (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.

[4] Ley, S. V.; Meerholz, C. A.; Barton, D. H. R. *Tetrahedron* **1981**, *37*, Suppl. No. 1, 213–223.

[5] (a) Detty, M. R.; Gibson, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 4086–4088. (b) Detty, M. R.; Gibson, S. L. *Organometallics* **1992**, *11*, 2147–2156.

[6] Detty, M. R.; Luss, H. R.; McKelvey, J. M.; Geer, S. M. *J. Org. Chem.* **1986**, *51*, 1692–1700.

[7] Detty, M. R. *Organometallics* **1991**, *10*, 702–712.

[8] (a) Detty, M. R.; Murray, B. J. *J. Org. Chem.* **1987**, *52*, 2123. (b) Detty, M. R.; Lenhart, W. C.; Gassman, P. G.; Callstrom, M. R. *Organometallics* **1989**, *8*, 861–865.

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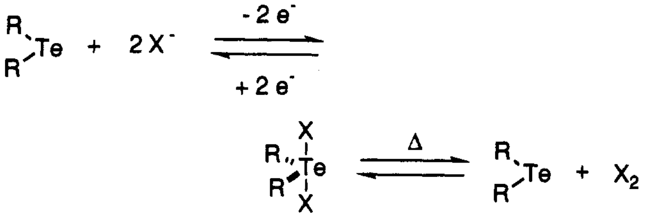
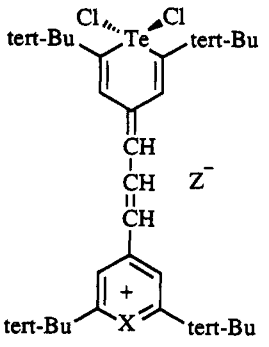
Scheme I



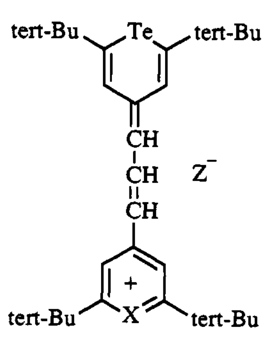
Scheme II

phenyltelluride[9] while Detty and Luss used line-shape analysis from variable-temperature ^{1}H NMR to follow tellurium–halogen exchange between tellurapyrylium dyes and dihalotellurium(IV) compounds derived from them.[10] In these studies, exchange pathways involving both second-order and first-order reactions were observed with two-electron changes in oxidation state, as summarized in Scheme II. Solvent polarity seemed to play an important mechanistic role in the Detty–Luss study in that the exchange reactions in acetonitrile were first order, while in tetrachloroethane the exchange reactions were second order.[10]

The description of intermediates or transition states for oxidative-addition and reductive-elimination reactions described above would be speculative, since scant data are available to describe these intermediates or transition states. Herein, we describe kinetic and mechanistic details of the reductive-elimination reactions of chlorine from dichlorotellurium(IV) species **2–5** in tetrachloroethane and acetonitrile. The kinetics of the reductive elimination were followed spectrophotometrically, allowing activation parameters to be calculated and solvent effects to be determined. The chloride ion was found to be a catalyst for the reductive elimination of chlorine from **2–5**.



2; X = Te, Z = Cl
3; X = Te, Z = PF$_6$
4; X = Se, Z = Cl
5; X = Se, Z = PF$_6$



6; X = Te, Z = Cl
7; X = Te, Z = PF$_6$
8; X = Se, Z = Cl
9; X = Se, Z = PF$_6$

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a General Electric QE-300 spectrophotometer or on a Varian Gemini-200 spectrophotometer. UV-visible–near infrared spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded on a Beckman IR 4250 instrument. Microanalyses were performed on a Perkin-Elmer 240 C, H, and N analyzer. Tellurapyrylium dyes **6–9** and selenapyrylium dyes **10** and **12** were prepared according to ref 11. Dichloromethane was obtained as anhydrous from Aldrich Chemical Co. and was used as received.

General Procedure for the Preparation of Te(IV) Dichlorides. A stock solution of chlorine in carbon tetrachloride was prepared by bubbling chlorine gas into the solvent. The weight of chlorine added was used to compute molarity (approximately 0.5 M). The chlorine solution (1.2–1.5 equiv) was added via syringe to the tellurapyrylium dye in dichloromethane (approximately 0.3 M). The resulting solution was stirred 15 min at ambient temperature and the Te(IV) dichloride was then precipitated with an equal volume of ether. The Te(IV) dichloride was collected by filtration, washed with ether, and dried.

For **2**: 89% yield of a maroon solid, mp 177–180 °C dec; ^{1}H NMR spectra are broadened by exchange (see ref 10); λ_{max} (CH$_2$Cl$_2$) 548 nm (ϵ 56 000 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{29}H_{43}Cl_2Te_2$·Cl: C, 46.24; H, 5.75. Found: C, 45.90; H, 5.46.

For **3**: 89% of a red solid, mp 185–188 °C dec; ^{1}H NMR spectra are broadened by exchange; see ref 10. λ_{max} (CH$_2$Cl$_2$) 548 nm (ϵ 55 000 L mol^{-1} cm^{-1}); IR (KBr) 2960, 1550 (s), 1470, 1365, 1313, 835 (s) cm^{-1}. Anal. Calcd for $C_{29}H_{43}Cl_2Te_2$·PF$_6$: C, 40.84; H, 5.08. Found: C, 40.90; H, 5.06.

For **4**: 89% of an orange-gold crystalline solid, mp 198–202 °C dec; λ_{max} (CH$_2$Cl$_2$) 535 nm (ϵ 59 000 L mol^{-1} cm^{-1}); ^{1}H NMR (CD$_3$CN) δ 8.64 (d × d, 1 H, J = 12, 15 Hz), 8.49 (s, 2 H), 7.18 (d, 1 H, J = 15 Hz), 7.05 (s, 1 H), 6.98 (d, 1 H, J = 12 Hz), 6.50 (s, 1 H), 1.61 (s, 18 H), 1.58 (s, 9 H), 1.50 (s, 9 H); IR (KBr) 2960, 1554, 1470, 1365, 1315, 1280, 1225, 1200 cm^{-1}. Anal. Calcd for $C_{29}H_{43}Cl_2$SeTe·Cl: C, 49.44; H, 6.15. Found: C, 49.44; H, 5.83.

For **5**: 80% of an orange-gold solid, mp 178–181 °C dec; λ_{max} (CH$_2$Cl$_2$) 532 nm (ϵ 60 000 L mol^{-1} cm^{-1}); ^{1}H NMR (CD$_3$CN) δ 8.59 (d × d, 1 H, J = 12, 15 Hz), 8.46 (s, 2 H), 7.16 (d, 1 H, J = 15 Hz), 7.025 (s, 1 H), 6.97 (d, 1 H, J = 12 Hz), 6.49 (s, 1 H), 1.61 (s, 18 H), 1.58 (s, 9 H), 1.50 (s, 9 H); IR (KBr) 2960, 1555, 1475, 1365, 963, 838 cm^{-1}. Anal. Calcd for $C_{29}H_{43}Cl_2$SeTe·PF$_6$: C, 43.16; H, 5.37. Found: C, 43.04; H, 5.33.

For **19**: 90% of a jet-black solid, mp 171–175 °C dec; λ_{max} (CH$_2$Cl$_2$) 530 nm (ϵ 48 000 L mol^{-1} cm^{-1}); ^{1}H NMR (CD$_3$CN) δ 8.34 (d, 1 H, J = 13.7 Hz), 8.14 (br s, 1 H), 7.75 (br s, 1 H), 7.58 (d, 1 H, J = 13.7 Hz), 7.21 (br d, 2 H), 7.03 (s, 1 H), 6.66 (s, 1 H), 3.61 (s, 6 H), 1.57 (s, 9 H), 1.52 (s, 9 H). Anal. Calcd for $C_{23}H_{32}Cl_2$NTe·PF$_6$: C, 41.48; H, 4.84; N, 2.10. Found: C, 41.17; H, 4.78; N, 2.12.

Preparation of Tellurapyrylium Dye 20. A mixture of 2,6-di-*tert*-butyl-4-methyltellurapyrylium hexafluorophosphate[11] (0.932 g, 2.00 mmol) and *p*-(*N*,*N*-dimethylamino)benzaldehyde (0.40 g, 2.5 mmol) in 5 mL of acetic anhydride was heated at reflux for 0.5 h. The reaction mixture was cooled to ambient temperature and was filtered through a pad of Celite. The filtrate was diluted with 100 mL of ether. The resulting solution was chilled, precipitating bright green crystals of **20**. The dye was collected by filtration, washed with ether, and dried to give 1.05 g (87%) of **20**, mp 210–211.5 °C: λ_{max} (CH$_2$Cl$_2$) 713 nm (ϵ 125 000 L mol^{-1} cm^{-1}); ^{1}H NMR (CD$_3$CN) δ 8.42 (d, 1 H, J = 15.5 Hz), 8.22 (s, 2 H), 7.77 (d, 2 H, J = 9.1 Hz), 7.34 (d, 1 H, J = 15.5 Hz), 6.85 (d, 2 H, J = 9.1 Hz), 3.08 (s, 6 H), 1.52 (s, 18 H). Anal. Calcd for $C_{23}H_{32}$NTe·PF$_6$: C, 46.42; H, 5.42; N, 2.35. Found: C, 46.87; H, 5.43; N, 2.38.

Preparation of Dye 11. Selenapyrylium dye **10** (5.85 g, 0.0100 mol) was dissolved in 200 mL of dichloromethane. To this solution was added 20 mL of a 0.50 M solution of chlorine in carbon tetrachloride (0.0100 mol). The resulting solution was stirred 3 min at ambient temperature and was concentrated.

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[9] (a) Nefedov, V. D.; Sinotova, E. N.; Sarbash, A. N.; Kolobov, E. A.; Kapustin, V. K. *Radiokhimiya* **1971**, *13*, 435–438. (b) Nefedov, V. D.; Sinotova, E. N.; Sarbash, A. N.; Timofev, S. A. *Radiokhimiya* **1969**, *11*, 154–156.

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The residue was recrystallized from 10% acetonitrile in ethyl ether to give 1.65 g (25%) of dye **11** as metallic green crystals, mp 170.5–172.5 °C: ^{1}H NMR (CDCl$_3$) δ 8.67 (s, 1 H), 8.13 (s, 4 H), 1.54 (s, 36 H); IR (KBr) 2960, 1586, 1465 (br, s), 1328, 1253, 1190, 1155, 675 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 177.8, 152.0, 136.5, 124.0, 123.8, 42.0, 31.8; λ_{max} (CH$_2$Cl$_2$) 802 nm (ϵ 150 000 L mol^{-1} cm^{-1}). Anal. Calc for $C_{29}H_{41}Cl_2Se_2{\cdot}Cl$: C, 53.27; H, 6.32; Cl, 16.26. Found: C, 53.21; H, 6.18; Cl, 16.50.

Preparation of Dye 13. Method A. Chloride salt **11** (0.97 g, 1.0 mmol) was dissolved in 50 mL of dichloromethane. Trifluoromethanesulfonic acid was added dropwise until the green color of the solution disappeared. The reaction mixture was washed with 150 mL of water. The organic phase was separated, dried over sodium sulfate, and concentrated. The residue was recrystallized from acetonitrile–ether to give 1.03 g (90%) of the triflate **13** as copper-bronze crystals, mp 181–182.5 °C: ^{1}H NMR (CDCl$_3$) δ 8.34 (s, 1 H), 8.01 (s, 4 H), 1.50 (s, 36 H); λ_{max} (CH$_2$Cl$_2$) 802 nm (ϵ 150 000 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{30}H_{41}Cl_2F_3O_3SSe_2$: C, 46.94; H, 5.38. Found: C, 46.96; H, 5.44.

Method B. Triflate dye **12** (1.20 g, 1.72 mmol) was dissolved in 50 mL of dichloromethane. To this solution was added 5.0 mL of a 0.4 M solution of chlorine in carbon tetrachloride (2.0 mmol). The resulting solution was stirred at ambient temperature for 5 min. The reaction mixture was concentrated, and the residue was recrystallized from 20 mL of acetonitrile diluted with 100 mL of ether. Upon chilling, 0.54 g (41%) of bronze crystals of **13** were collected, mp 180–182 °C: ^{1}H NMR (CDCl$_3$) δ 8.365 (s, 1 H), 8.03 (s, 4 H), 1.52 (s, 36 H); λ_{max} (CH$_2$Cl$_2$) 802 nm (ϵ 150 000 L mol^{-1} cm^{-1}).

The mother liquors were concentrated to approximately one-third volume to give 0.052 g (4%) of a second crop containing mostly monochloro dye **14**: ^{1}H NMR (CDCl$_3$) δ 8.83 (d, 1 H), 8.015 (s, 4 H), 6.92 (d, 1 H), 1.50 (s, 36 H).

Preparation of 15. Triflate dye **12** (1.20 g, 1.72 mmol) was dissolved in 50 mL of dichloromethane. To this solution was added 5.0 mL of a 0.4 M solution of bromine in carbon tetrachloride (2.0 mmol). The resulting solution was stirred at ambient temperature for 5 min. The reaction mixture was concentrated, and the residue was recrystallized from 20 mL of acetonitrile diluted with 100 mL of ether. Upon chilling, 0.07 g (<5%) of bronze crystals of **15** were collected, mp 165–175 °C dec: ^{1}H NMR (CDCl$_3$) δ 8.34 (s, 1 H), 7.95 (s, 4 H), 1.45 (s, 36 H); λ_{max} (CH$_2$Cl$_2$) 752 nm (ϵ 215 000 L mol^{-1} cm^{-1}). We were unable to obtain a satisfactory analysis for this material presumably due to a mixture of tribromide and triflate counterions.

Kinetics Procedures for Reductive Eliminations of Te(IV) Dihalides in Tetrachloroethane. Tetrachloroethane was distilled from barium oxide and stored over 3-Å molecular sieves. Approximately 5×10^{-6} M solutions of the Te(IV) dihalides in tetrachloroethane were prepared in 100.0-mL volumetric flasks. Solutions of tetra-*n*-butylammonium chloride and tetra-*n*-butylammonium fluoroborate were prepared at 1.0×10^{-3} M in tetrachloroethane. The ammonium salts were dried at 60 °C and 0.1 Torr for 24 h prior to use. The ammonium salt solutions were added to Te(IV) dihalide to give 5×10^{-6} M solutions of dihalide in 1.0×10^{-3} M ammonium salt.

Kinetic measurements were made on a Perkin-Elmer 330 spectrophotometer equipped with a digital temperature controller for 1-cm cells. The absorption spectra from 900 to 400 nm were scanned repetitively for at least 3 half-lives. Infinity runs were determined after >7 half-lives. Rate constants were determined for both appearance of reduced dye and disappearance of oxidized dye. These numbers agreed within 5% for all runs. Duplicate runs of the kinetics gave rate constants that agreed within 5%.

Calculation of First-Order Rate Constants. Relative absorbance measurements, [Abs]$_t$, during the first and second half-lives were measured at regular time intervals. The absorbance at infinity, [Abs]$_\infty$, was measured at the wavelength of both oxidized and reduced dye. From the first-order rate expression

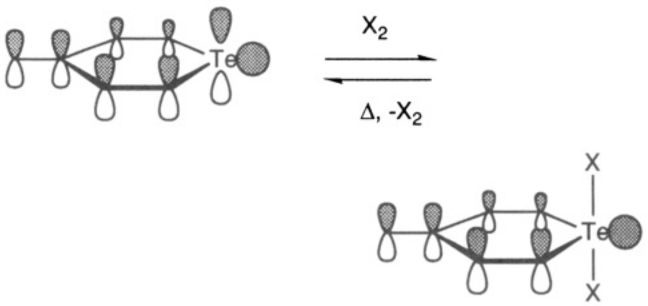
$$\ln\,[[\mathrm{Abs}]_\infty - [\mathrm{Abs}]_t] = k_1 t$$

for the appearance of reduced dye and

$$\ln\,[[\mathrm{Abs}]_t - [\mathrm{Abs}]_\infty] = k_1 t$$

for the loss of oxidized dye. The slope of a plot of ln [Abs] vs *t* gave *k*.

Scheme III



Calculation of Activation Parameters. Arrhenius parameters were obtained by plotting ln *k* against 1/*T*, with a slope equal to the energy of activation divided by the gas constant, E_a/R, and an intercept equal to the preexponential factor, ln *A*. Eyring activation parameters were determined using transition-state theory. A plot of $R \ln (k/T) + \ln (Nh/R)$ versus $1/T$ gives a linear slope equal to $-\Delta H^{\ddagger}$ and an intercept of $\Delta S^{\ddagger}$, where *N* is Avogadro's number, *h* is Plank's constant, $\Delta H^{\ddagger}$ is the enthalpy of activation, and $\Delta S^{\ddagger}$ is the entropy of activation.

Rate Constants in Catalyzed Reactions. In those reactions in which chloride is a catalyst, the rate equation must account for both the catalyzed and uncatalyzed reactions:

$$-\mathrm{d}[\mathrm{Abs}]/\mathrm{d}t = k_{\mathrm{cat}}[\mathrm{cat}][\mathrm{Abs}] + k_1[\mathrm{Abs}]$$

which is equivalent to:

$$-\mathrm{d}[\mathrm{Abs}]/[\mathrm{Abs}]\mathrm{d}t = k_{\mathrm{app}} = k_{\mathrm{cat}}[\mathrm{cat}] + k_1$$

The rate of the catalytic reaction, k_{cat}, is determined by measuring the apparent rate constant, k_{app}, and knowing both the catalyst concentration ([cat]) and k_1, the first-order rate constant. A pseudo-first-order rate constant was observed when chloride was introduced as a catalyst for the reductive elimination of chlorine from Te(IV) dichlorides **2–5**.

Results and Discussion

Oxidative Addition of Halogens to Tellurapyrylium Dyes. The dihalotellurium(IV) species **2–5** were prepared by the oxidative addition of chlorine to the appropriate tellurapyrylium dye **6–9**.[10] A standard solution of chlorine in carbon tetrachloride was prepared. A slight excess of chlorine was then added to dichloromethane solutions of the tellurapyrylium dyes **6–9** giving products which were isolable crystalline solids.

The oxidative addition of halogens or hydrogen peroxide across a tellurium atom of tellurapyrylium dyes **6–9** removes a tellurium-atom p-orbital from conjugation with the carbon π-framework via formation of a trigonal bipyramid with the halo ligands in the axial positions (Scheme III).[10] While the tellurapyrylium dyes **6–9** absorb in the near infrared [λ_{max} of 828 nm in dichloromethane for **6** and **7** (ϵ 330 000 L mol^{-1} cm^{-1}) and 786 nm in dichloromethane for **8** and **9** (ϵ 280 000 L mol^{-1} cm^{-1})], the tellurium(IV) species **2–5** absorb at much shorter wavelengths (approximately 550 nm for **2** and **3** and 535 nm for **4** and **5** with ϵ >50 000 L mol^{-1} cm^{-1}). The differences in absorption spectra would permit facile monitoring of the disappearance of one chromophore with the appearance of the other.

Heating solutions of dichlorotellurium(IV) species **2–5** resulted in loss of the chromophore associated with **2–5**

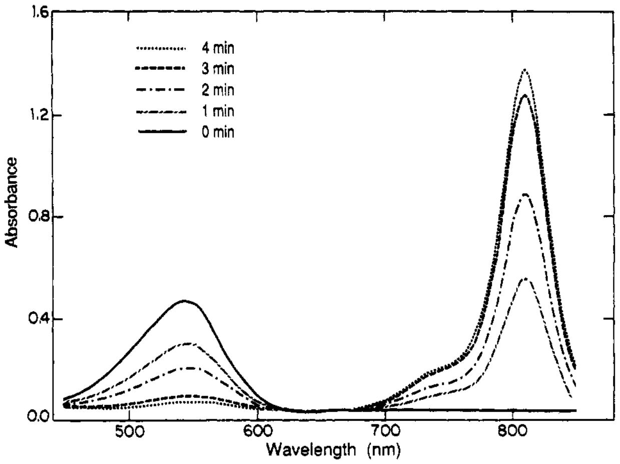


Figure 1. Absorption spectra during the course of reductive elimination of chlorine from dichlorotellurium(IV) compound **2** in tetrachloroethane solution at 373 K.

and appearance of the chromophore of the reduced tellurapyrylium dye **6–9**. Presumably, this process involved the reductive elimination of chlorine from dichlorotellurium(IV) dyes **2–5**. This process is shown in Figure 1 for the reductive elimination of chlorine from **2** in tetrachloroethane solution at 373 K. Isosbestic behavior was observed in these reactions, as shown in Figure 1, with an isosbestic point at 635 nm.

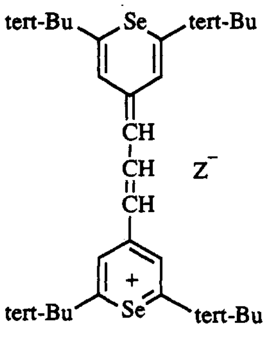
Reaction of Halogens with Selenapyrylium Dyes. Oxidative addition reactions of halogens with the selenium atoms of selenapyrylium dyes have not been reported. Since neutral dihalodiorganoselenium(IV) derivatives are common, we felt that similar products might be isolated with selenapyrylium dyes. Much to our surprise, products isolated from the addition of halogen to selenapyrylium species were a result of halogen addition to carbon–carbon double bonds.

The addition of 1.0 equiv of chlorine to chloride salt **10** in dichloromethane gave a 25% yield of dichloride **11** as a dark green crystalline solid. The ^1H NMR spectrum of **11** is quite simple, consisting of three singlets at δ 8.70 (1 H), 8.13 (4 H), and 1.54 (36 H). The ^{13}C NMR spectrum also confirms the symmetry of **11** with lines at δ 177.8, 152.0, 136.5, 124.0, 123.8, 42.0, and 31.8. The absorption spectrum of **11** in dichloromethane gives λ_{max} of 802 nm (ϵ 150 000 L mol^{-1} cm^{-1}).

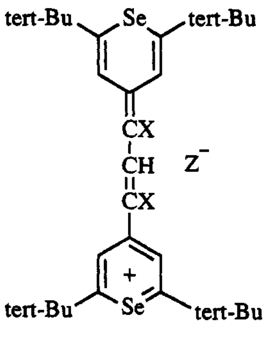
The addition of 1.0 equiv of chlorine to trifluoromethanesulfonate salt **12** gave dichloride **13** in 41% isolated yield as bronze crystals. In this reaction, small amounts of the monochloro product **14** were detected by ^1H NMR with one-proton doublets centered at δ 8.83 and 6.92, two-proton singlets at δ 8.015 and 7.99, and a 36-proton singlet at δ 1.50. However, the monochloro product was not isolated in pure form.

The addition of 1.0 equiv of bromine to **12** gave small amounts of a product (<5%) whose ^1H NMR spectrum was consistent with dibromide **15** with a one-proton singlet at δ 8.34, a four-proton singlet at δ 7.95, and a 36-proton singlet at δ 1.45. The absorption spectrum of **15** was somewhat broadened relative to **12** although λ_{max} was relatively unchanged with λ_{max} of 752 nm for **15** in dichloromethane (ϵ 215 000 L mol^{-1} cm^{-1}) and 748 nm for **12** in dichloromethane (ϵ 265 000 L mol^{-1} cm^{-1}).

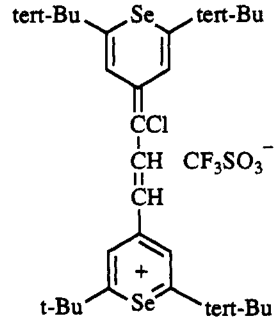
Kinetic Analysis of the Thermal Reductive Elimination of Chlorine from Te(IV) Dichlorides 2–5 in Tetrachloroethane Solution. Rate constants, k_1, for the disappearance of the chromophore of dichlorotellurium(IV) compounds **2–5** were measured at several temperatures in tetrachloroethane. First-order behavior was observed for both the disappearance of the Te(IV) species as well as for the appearance of the tellurapyrylium dye over at least 3 half-lives. One or more duplicate runs were performed at each temperature and rate constants agreed within 5%. Rate constants are compiled in Table I.



10, Z = Cl
12, Z = CF_3SO_3



11; X = Cl, Z = Cl
13; X = Cl, Z = CF_3SO_3
15; X = Br, Z = CF_3SO_3



14

From the rate constants listed in Table I, values for both the Arrhenius activation parameters (E_a and ln A) and the Eyring enthalpy (ΔH^*) and entropy (ΔS^*) of activation can be determined. These values are also compiled in Table I and are similar in magnitude in all four systems.

At 298 K, values of ΔG^* were calculated to be 18.2 kcal mol^{-1} for **2**, 19.3 kcal mol^{-1} for **3**, 17.8 kcal mol^{-1} for **4**, and 19.5 kcal mol^{-1} for **5**. For both pairs of Te(IV) dye structures, ΔG^*_{298K} was lower for the chloride salt relative to the hexafluorophosphate salt (1.1 kcal mol^{-1} for **2** and 1.7 kcal mol^{-1} for **4**). Although the observed reactions followed first-order behavior, these observations suggest that the chloride ion is involved in the rate-determining step of the reductive elimination of chlorine in these systems, perhaps in the role of catalyst.

To test the hypothesis that the chloride ion is a catalyst in the reductive elimination of chlorine in the Te(IV) dichlorides, the rates of disappearance of chloride salt **2** and hexafluorophosphate salt **3** (5×10^{-6} M in dye) were measured in the presence of 0.001 M tetra-*n*-butylammonium chloride in tetrachloroethane. The observed rate constants as well as the appropriate Eyring parameters are compiled in Table II. The disappearance of the chromophore of **3** was also measured in 0.001 M tetra-*n*-butylammonium fluoroborate in tetrachloroethane to give constant ionic strength (relative to the tetra-*n*-butylammonium chloride solutions) in the presence of a presumably inert counterion.

Table I. Rate Constants and Arrhenius and Eyring Activation Parameters for Reductive Elimination of Chlorine from Tellurapyrylium Dichloride Dyes 2–5 and 19 in Tetrachloroethane

compd	*T*, K	*k*, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	E_a, kcal mol^{-1}	ln *A*
2	333.0	$(9.76 \pm 0.01) \times 10^{-5}$	20.6 ± 0.5	8 ± 1	21.3 ± 0.5	23.0
	348.0	$(4.44 \pm 0.01) \times 10^{-4}$				
	363.0	$(1.41 \pm 0.03) \times 10^{-3}$				
3	323.0	$(4.92 \pm 0.01) \times 10^{-6}$	21.4 ± 0.3	7 ± 2	22.3 ± 0.3	22.3
	348.0	$(5.20 \pm 0.01) \times 10^{-5}$				
	373.0	$(4.99 \pm 0.08) \times 10^{-4}$				
4	323.0	$(8.54 \pm 0.02) \times 10^{-5}$	22.6 ± 0.2	16 ± 6	23.3 ± 0.2	26.9
	338.0	$(4.45 \pm 0.02) \times 10^{-4}$				
	348.0	$(1.20 \pm 0.02) \times 10^{-3}$				
	363.0	$(4.61 \pm 0.02) \times 10^{-3}$				
5	348.0	$(7.17 \pm 0.00) \times 10^{-5}$	23.4 ± 0.2	13 ± 4	24.1 ± 0.2	25.4
	363.0	$(3.20 \pm 0.02) \times 10^{-4}$				
	378.0	$(1.17 \pm 0.04) \times 10^{-3}$				
19	340.5	$(5.31 \pm 0.10) \times 10^{-4}$	16.8 ± 0.5	−1 ± 3	17.5 ± 0.5	18.5
	348.0	$(1.15 \pm 0.02) \times 10^{-3}$				
	353.0	$(1.42 \pm 0.03) \times 10^{-3}$				
	358.0	$(1.94 \pm 0.04) \times 10^{-3}$				
	363.0	$(2.78 \pm 0.08) \times 10^{-3}$				
	368.0	$(3.75 \pm 0.10) \times 10^{-3}$				
	370.5	$(5.01 \pm 0.12) \times 10^{-3}$				

Table II. Rate Constants and Arrhenius and Eyring Activation Parameters for Reductive Elimination of Chlorine from Tellurapyrylium Dichloride Dyes 2 and 3 in the Presence of Added Tetra-*n*-butylammonium Chloride and Added Tetra-*n*-butylammonium Fluoroborate

compd	*T*, K	*k*, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{298K}$, kcal mol^{-1}
2			20.6 ± 0.5	8 ± 1	18.2
2 + 0.001 M *n*-$Bu_4N^+Cl^-$	333.0	$(1.75 \pm 0.01) \times 10^{-4}$	20.4 ± 0.2	9 ± 2	17.7
	363.0	$(2.44 \pm 0.04) \times 10^{-3}$			
3			21.4 ± 0.3	7 ± 2	19.3
3 + 0.001 M *n*-$Bu_4N^+Cl^-$	333.0	$(1.76 \pm 0.01) \times 10^{-4}$	21.9 ± 0.1	13 ± 1	18.0
	348.0	$(7.70 \pm 0.02) \times 10^{-4}$			
	363.0	$(2.95 \pm 0.01) \times 10^{-3}$			
3 + 0.001 M *n*-$Bu_4N^+BF_4^-$	333.0	$(6.69 \pm 0.01) \times 10^{-6}$	23.2 ± 0.3	11 ± 2	19.9
	373.0	$(3.22 \pm 0.11) \times 10^{-4}$			

Both **2** and **3** gave nearly identical rate constants in the presence of 0.001 M tetra-*n*-butylammonium chloride in tetrachloroethane (1.75×10^{-4} and 1.76×10^{-4} s^{-1}, respectively) at 333 K. In the presence of 0.001 M tetra-*n*-butylammonium fluoroborate in tetrachloroethane, the rate constant for reductive elimination of chlorine with **3** is nearly 30-fold slower (6.69×10^{-6} s^{-1}) at 333 K, which is indicative that ionic strength is not contributing to the observed acceleration with added chloride.

From the Eyring parameters listed in Table II, the reductive elimination of chlorine in the presence of 0.001 M tetra-*n*-butylammonium chloride proceeds with $\Delta G^{\ddagger}_{298K}$ nearly 2 kcal mol^{-1} lower than that in the presence of 0.001 M tetra-*n*-butylammonium fluoroborate. Again, this is consistent with chloride catalysis in the reductive elimination.

Kinetic Analysis of the Thermal Reductive Elimination of Chlorine from Te(IV) Dichlorides 3–5 in Acetonitrile Solution. Stock solutions of **3**–**5** in acetonitrile (freshly distilled from calcium hydride) were prepared. The appearance of the tellurapyrylium dye and the disappearance of the Te(IV) dichloride dye were monitored in the spectrophotometer as a function of time. First-order behavior was only observed for the first 2 half-lives for loss of the chromophore for the dichlorotellurium(IV) species **3** and **5** or for the appearance of the corresponding tellurapyrylium dyes. Dichlorotellurium(IV) dye **4** showed first-order behavior throughout the reductive elimination. The rate of reaction accelerated with **3** and **5** as the reductive elimination neared completion, suggesting an autocatalytic pathway. Initial rate constants (1 half-life for **3** and **5**, 2 half-lives for **4**) and Arrhenius and Eyring activation parameters are compiled in Table III for **3**–**5**. Due to the lower boiling point of acetonitrile relative to tetrachloroethane, the temperature range explored in acetonitrile was smaller.

Table III. Rate Constants and Arrhenius and Eyring Activation Parameters for Reductive Elimination of Chlorine from Tellurapyrylium Dichloride Dyes 3–5 in Acetonitrile

compd	*T*, K	*k*, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	E_a, kcal mol^{-1}	ln *A*
3	328.0	$(1.33 \pm 0.01) \times 10^{-5}$	20.0 ± 0.5	4 ± 3	20.7 ± 0.5	20.6
	348.0	$(8.25 \pm 0.01) \times 10^{-5}$				
4	348.0	$(3.93 \pm 0.02) \times 10^{-3}$				
5	318.0	$(3.25 \pm 0.01) \times 10^{-6}$	23.1 ± 0.5	12 ± 4	23.8 ± 0.5	25.0
	333.0	$(1.78 \pm 0.01) \times 10^{-5}$				
	348.0	$(8.11 \pm 0.05) \times 10^{-5}$				

Values of the Arrhenius activation energy, E_a, and the Eyring enthalpy of activation, $\Delta H^{\ddagger}$, are slightly lower in acetonitrile relative to tetrachloroethane for both **3** and **5**. The rates of reaction are only slightly faster for the hexafluorophosphate salts in acetonitrile relative to tetrachloroethane at a common temperature for both **3** (5.20×10^{-5} s^{-1} in tetrachloroethane and 8.25×10^{-5} s^{-1} in acetonitrile at 348 K, Table III) and **5** (7.17×10^{-5} s^{-1} in tetrachloroethane and 8.11×10^{-5} s^{-1} in acetonitrile at 348 K, Table III). Due to the smaller range of temperatures for the kinetic studies in acetonitrile, the uncertainty in values of $\Delta S^{\ddagger}$ are larger than in tetrachloroethane which leads to greater uncertainty in calculations of values of $\Delta G^{\ddagger}_{298K}$. Calculated values of $\Delta G^{\ddagger}_{298K}$ in tetrachloroethane are 19.3 kcal mol^{-1} for **3** and 19.5 kcal mol^{-1} for **5**. In acetonitrile, these values are 18.8 kcal mol^{-1} for **3** and 19.5 kcal mol^{-1} for **5**.

Chloride catalysis was more pronounced in acetonitrile than in tetrachloroethane. Reductive elimination of chlorine from chloride salt **4** was nearly 50-fold faster than from hexafluorophosphate salt **5** at 348 K (3.93×10^{-3} s^{-1} for **4** and 8.11×10^{-5} s^{-1} for **5**) in acetonitrile. The rate of reductive elimination of chlorine from **4** was 3-fold faster in acetonitrile at 348 K (3.93×10^{-3} s^{-1}) relative to tetrachloroethane (1.20×10^{-3} s^{-1}).

Discussion of Mechanistic Considerations in the Reductive Elimination of Chlorine from 2–5. Although few mechanistic studies of oxidative-addition and reductive-elimination reactions of organotellurium compounds have been described, the analogous chemistry in oxidative additions of halogens to platinum(II) and reductive eliminations from platinum(IV) has been described.[12–14] Among the mechanistic possibilities explored in this chemistry have been the possibility of synchronous oxidative addition of halogen across platinum[12,13] or the

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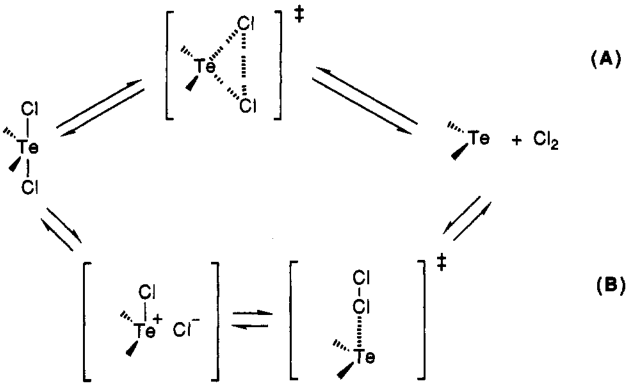
(12) van Koten, G.; Terheijden, J.; van Beek, J. A. M.; Wehman-Ooyevaar, I. C. M.; Muller, F.; Stam, C. H. *Organometallics* **1990**, *9*, 903–912.

(13) (a) Braterman, P. S.; Cross, R. J. *Chem. Soc. Rev.* **1973**, *2*, 271. (b) Pearson, R. G. *Pure Appl. Chem.* **1971**, *27*, 145.

(14) (a) Skinner, C. E.; Jones, M. M. *J. Am. Chem. Soc.* **1969**, *91*, 4405–4408. (b) Jones, M. M.; Morgan, K. A. *J. Inorg. Nucl. Chem.* **1972**, *34*, 259–274. (c) Morgan, K. A.; Jones, M. M. *J. Inorg. Nucl. Chem.* **1972**, *34*, 275–296. (d) Hopgood, D.; Jenkins, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 4461–4463. (e) Elding, L. I.; Gustafson, L. *Inorg. Chim. Acta* **1976**, *19*, 165–171. (f) van Beek, J. A. M.; van Koten, G.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5010–5011.

Scheme IV



possibility of stepwise formation of an η^1-complex of halogen with platinum followed sequentially by oxidative addition and formation of the second platinum-halogen bond.[12,14]

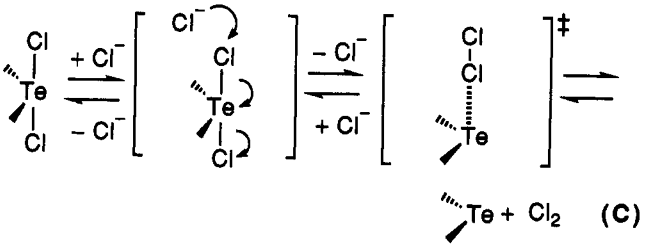
Analogues of these two mechanistic possibilities are shown in Scheme IV for oxidative-addition and reductive-elimination reactions of chlorine with organotellurium compounds. A unimolecular reductive elimination of chlorine would presumably involve simultaneous formation of the chlorine–chlorine bond and breaking of the tellurium–chlorine bonds (Scheme IV, path A). Little charge generation should be observed along the reaction coordinate of this path. The formation of two molecules from one molecule would contribute to the large, positive entropy of activation. If path B (Scheme IV) were followed, heterolytic cleavage of one tellurium–chlorine bond would lead to a charged intermediate. Subsequent attack of chloride at the chloro ligand would lead to cleavage of the second tellurium–chlorine bond as well as reduce the tellurium center from tellurium(IV) to tellurium(II). Again, the formation of two species from one should contribute to a large, positive entropy of activation.

The principal of microscopic reversibility would suggest the reverse of paths A and B would be true for oxidative addition. Thus, path A represents a concerted oxidative addition of chlorine across tellurium with synchronous cleavage of the chlorine–chlorine bond, oxidation of tellurium(II) to tellurium(IV), and formation of the tellurium–chlorine bonds while path B suggests the formation of an η^1-complex of chlorine and tellurium(II) followed by stepwise formation of one tellurium–chlorine bond with oxidation and then formation of the second tellurium–chlorine bond.

Mechanistically, the change in solvents from tetrachloroethane to acetonitrile has a small effect on the rate of reductive elimination of chlorine from **3** or **5** as measured by either the first-order rate constants (k_1) or the activation parameters (Table III). While rates of reaction are only slightly faster in acetonitrile than in tetrachloroethane in the temperature range of this study, values of E_a and $\Delta H^{\ddagger}$ are lower by 1.5 and 1.4 kcal mol^{-1}, respectively, for **3** and are each lower by 0.3 kcal mol^{-1} for **5** in acetonitrile.

If charged intermediates were involved, as shown in path B of Scheme IV, acetonitrile would be expected to have a stabilizing role on developing or fully developed charges. Alternatively, a concerted reaction, as depicted in path A, would develop little formal charge along the reaction coordinate and the effects of a change in solvent polarity would be less pronounced. Since the effect of solvent polarity is small, a transition state as depicted in path A of Scheme IV is consistent with the observed results.

Scheme V



However, path B of Scheme IV cannot be rigorously excluded. Some increase in rate is observed, and values of E_a and $\Delta H^{\ddagger}$ are somewhat smaller in acetonitrile. Paths A and B may both be operative in acetonitrile with similar values of $\Delta G^{\ddagger}$ at any given temperature employed in this study. In NMR studies of tellurium–halogen exchange reactions with tellurapyrylium dyes, a second-order process was observed in tetrachloroethane and a first-order process was observed in acetonitrile.[10]

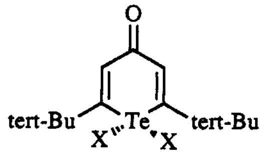
The acceleration of rate with time in acetonitrile for the reductive elimination of chlorine from **3** and **5** is consistent with either the generation of chloride ion as a catalyst as a function of time or with a change in mechanism as the concentration of reduced tellurapyrylium dye **7** or **9** increases as a function of time.

Chloride appears to function as a catalyst in the reductive-elimination reactions observed for **2**–**5**. From the apparent first-order rate constants at 348 K (Table I), k_{cat} for chloride is calculated to be 7.60×10^1 mol^{-1} s^{-1} with **2** and **3** and is calculated to be 2.26×10^2 mol^{-1} s^{-1} with **4** and **5** when measured for 5×10^{-6} M chloride in tetrachloroethane. At 348 K, relative rate ratios for the catalyzed and uncatalyzed pathways are 7.54 for **2** and **3** and 15.8 for **4** and **5**. In acetonitrile at 348 K, k_{cat} for chloride with **4** and **5** is calculated to be 7.62×10^2 mol^{-1} s^{-1} and the relative rate ratio is 47.0. A 3-fold increase in the rate of catalysis in acetonitrile relative to tetrachloroethane is consistent with more polar intermediates or transition states in the catalyzed reaction versus the noncatalyzed reaction.

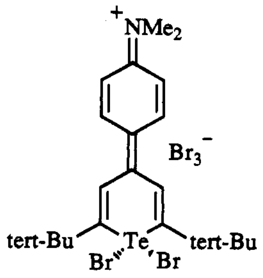
One possible mechanistic path for chloride catalysis is illustrated in Scheme V as path C. This pathway resembles path A of Scheme IV in that a synchronous—albeit via a second-order reaction—cleavage of both tellurium–chlorine bonds might be accompanied by reduction of tellurium(IV) to tellurium(II) and resembles path B in that either an η^1-complex of chlorine and tellurium(II) or a linear alignment of reacting atoms is involved in tellurium–chlorine bond cleavage. The negative charge added by the approach of chloride would be stabilized in acetonitrile relative to tetrachloroethane, which is reflected in the 3-fold increase in rate of catalysis in acetonitrile. Conversely, a chloride-catalyzed oxidative addition would follow the reverse of Scheme V.

Attempted Reductive Elimination Reactions in Neutral Tellurium(IV) Species. The neutral tellurapyranone dihalide derivatives **16** and **17** have been prepared.[8a] At 400 K, tetrachloroethane solutions of these materials were thermally much more stable than the solutions of **2**–**5**. No reductive elimination of halogen from solutions of **16** and **17** was detected spectrophotometrically after 4 h.

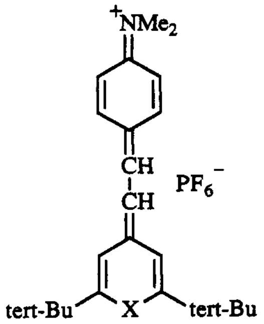
The question arises as to why reductive elimination occurs much more readily in the cationic dyes **2**–**5** relative to the neutral derivatives **16** and **17**. The oxidative



16, X = Cl
17, X = Br



18



19, X = $TeCl_2$
20, X = Te

addition across tellurium to give **2**–**5** would disrupt the aromaticity of the tellurapyrylium ring in dyes **6**–**9**. The energetics of this disruption would then determine the rate of reductive elimination as well as the rate of oxidative addition.

The disruption of benzenoid aromaticity has been observed experimentally in the X-ray crystal structure of aniline dye **18**.[10] Alternate single (1.44 Å) and double (1.35 Å) bonds were observed in the anilinium component as well as the tellurapyranyl component of structure **18**. The double bond linking the two rings was somewhat long at 1.40 Å.

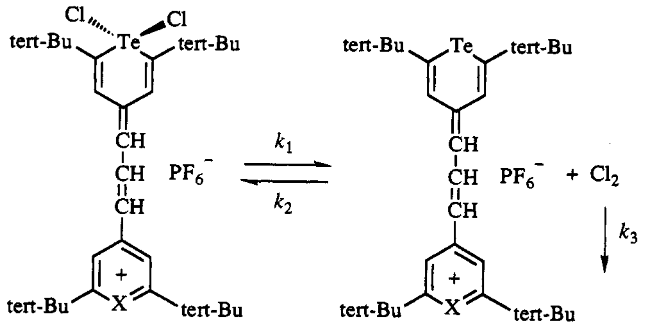
The anilinium dye **19** was prepared by oxidative addition of chlorine across the tellurium atom of tellurapyrylium dye **20**. The anilinium dye **19** is a two-carbon homologue of **18** and, like **18**, oxidative addition across tellurium would disrupt the aromaticity of a benzenoid ring.

Kinetic Analysis of the Thermal Reductive Elimination of Chlorine from Te(IV) Dichloride 19 in Tetrachloroethane Solution. A stock solution of the dichloride **19** was prepared in tetrachloroethane. Upon heating, the chromophore associated with Te(IV) dichloride **19** decreased in intensity while the chromophore associated with reduced tellurapyrylium dye increased in intensity. Rate constants and Arrhenius and Eyring activation parameters for **19** are compiled in Table I.

From the activation parameters measured for **19**, ΔG^{*}_{298K} in tetrachloroethane is calculated to be 17.1 kcal mol^{-1}, significantly lower than ΔG^{*}_{298K} of 19.3 and 19.5 kcal mol^{-1} for the Te(IV) dichlorides **3** and **5**, respectively. Disruption of the aniline ring in **19** should be energetically more costly than disruption of the aromaticity of a tellurapyrylium nucleus in **3** and **5**. Reductive elimination of chlorine from **19** regenerates the aniline ring, which should be energetically more favorable than regenerating a tellurapyrylium ring in **3** and **5** (where an aromatic heterocyclic residue remains even after oxidative addition across tellurium). Values of ΔH^{*} and E_a for reductive elimination of chlorine in **19** (ΔH^{*} = 16.8 kcal mol^{-1}, E_a = 17.5 kcal mol^{-1}) are lower relative to **3** (ΔH^{*} = 21.4 kcal mol^{-1}, E_a = 22.3 kcal mol^{-1}) and **5** (ΔH^{*} = 23.4 kcal mol^{-1}, E_a = 24.1 kcal mol^{-1}), values consistent with this argument.

The Eyring entropy of activation (ΔS^{*}) is significantly more negative for **19** (−1 cal mol^{-1} K^{-1}) than those observed for **3** (7 cal mol^{-1} K^{-1}) and **5** (13 cal mol^{-1} K^{-1}). This is perhaps indicative of an earlier transition state in the reductive elimination of chlorine from **19** as a consequence of participation of the carbon π-framework along path A of Scheme IV.

Scheme VI



Equilibria Involving Oxidative Addition and Reductive Elimination. The preparation of the dichlorotellurium(IV) dyes involves high concentrations of chlorine and tellurapyrylium dye (approximately 0.1 M) relative to the concentrations employed in the studies of the kinetics of reductive elimination (approximately 10^{-5} M). The reaction equilibria for these reactions are summarized in Scheme VI. The isolation of the dichlorotellurium(IV) products must be due to kinetic control at the concentrations employed and suggest that values of k_2 are reasonably large.

The second-order rate constant for the oxidative addition of hydrogen peroxide to tellurapyrylium dyes **6**–**9** is on the order of 1–2 M^{-1} s^{-1}.[7] The oxidative addition of chlorine to tellurapyrylium dyes **6**–**9** appears to be much faster. A stock solution of tellurapyrylium dye **9** (1.0 × 10^{-5} M) in tetrachloroethane was prepared. Aliquots of a 5.0 × 10^{-2} M solution of chlorine in carbon tetrachloride were added to the stock solution at 298 K to give initial chlorine concentrations of 5.0 × 10^{-6}, 1.0 × 10^{-5}, and 2.0 × 10^{-5} M. The formation of **5** was complete at 298 K within 60 s, and where an excess of chlorine was used, no **9** was detected. At 5.0 × 10^{-6} M chlorine, half of the absorbance of **9** was lost, while at 1.0 × 10^{-5} M chlorine, more than 95% of the absorbance associated with **9** was lost. Corresponding concentrations of oxidized dye were 5.0 × 10^{-6} and 1.0 × 10^{-5} M, respectively, based on absorbance. With tellurapyrylium dye as limiting reagent (2.0 × 10^{-5} M chlorine), the equilibrium concentration of **9** is less than 1 × 10^{-9} M (based on an optical density of ≤0.003 at 790 nm in a 10-cm cell). It was assumed that the equilibrium chlorine concentration was equal to the initial concentration minus the concentration of **5** (1.0 × 10^{-5} M). The rate constant for reductive elimination, k_1, at 298 K was calculated from the Arrhenius activation parameters to be 1.8 × 10^{-7} s^{-1}. From these data, the second-order rate constant, k_2, was calculated to be ≥1.8 × 10^{3} mol^{-1} s^{-1} on the basis of the spectroscopic data at equilibrium and ≥10^{4} mol^{-1} s^{-1} on the basis of the rate of appearance of **5** (assuming $t_{1/2} \leq 10$ s).

In view of the magnitude of k_2 relative to k_1, chlorine must be removed from the system as it is produced in order for reductive elimination to go to completion at room

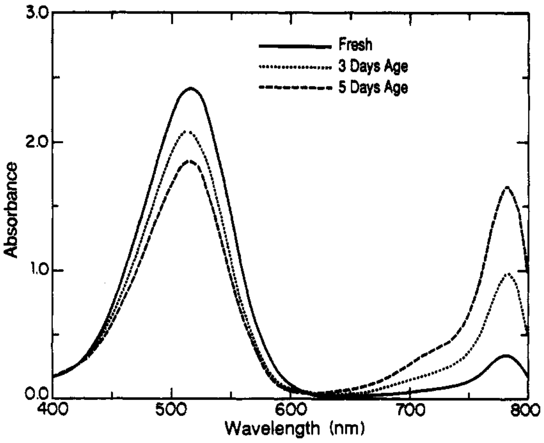


Figure 2. Effects of aging at ambient temperature of a 0.015 M solution of **5** in HMP for 5 days. The 0.015 M solution was diluted 100-fold with HMP to give the observed spectra.

temperature and presumably at higher temperatures (although the temperature dependence of k_2 has not been addressed). This path is characterized by k_3 in Scheme VI. Loss of chlorine to the atmosphere, reaction of chlorine with tetrachloroethane (or traces of olefin material in the solvent) or acetonitrile, and reaction of chlorine with the trimethine bridge of **9** (analogous to the chlorination of **10** or **12**) might all contribute to the magnitude of k_3.

Stock solutions of chlorine at 1×10^{-5} M in tetrachloroethane were prepared, and the lifetime of chlorine in the solvent at 333 and 348 K was determined. The concentration of chlorine was monitored by titration of aliquots with tellurapyrylium dye **9** to give tellurium(IV) dichloride **5**. At 333 K, the half-life of chlorine was less than 10 min, while at 348 K, the half-life of chlorine was less than 3 min. It follows that the first-order or pseudo-first-order rate constant for loss of chlorine from the system is $\geq 1 \times 10^{-3}$ s^{-1} at 333 K and $\geq 4 \times 10^{-3}$ s^{-1} at 348 K. These data suggest that $k_3 \gg k_1$ and that k_3, as shown in Scheme VI, is not the rate-determining step in the reductive elimination reaction.

The addition of 0.1 M cyclohexene had negligible effect on the observed rates of reductive elimination of chlorine from **5** in tetrachloroethane. At 348 K, k_1 for **5** in tetrachloroethane with added cyclohexene was 7.30×10^{-5} s^{-1}.

Equilibria in 4-Hydroxy-4-methyl-2-pentanone. In other solvent systems, the equilibrium constants for the reaction in Scheme VI are much larger and both tellurium(II) and tellurium(IV) species can be observed spectroscopically at equilibrium. In alcoholic solvents such as 4-hydroxy-4-methyl-2-pentanone (HMP), solutions containing only the tellurium(IV) dichloride **5** at 0.015 M established an equilibrium after several days at ambient temperature. The chromophores of both **5** and the reduced dye **9** were observed. The absorption spectra shown in Figure 2 were obtained after the 0.015 M dye solution was diluted 100-fold with HMP.

When the aged 0.015 M solution of **5** in HMP is diluted 100-fold with dichloromethane, the chromophore associated with **9** disappears with time while the chromophore associated with **5** increases in intensity, as shown in Figure 3. This is consistent with a different equilibrium constant in dichloromethane relative to that in HMP. And free chlorine present in the HMP solution reoxidizes tellurium(II) to tellurium(IV) when diluted with dichloromethane.

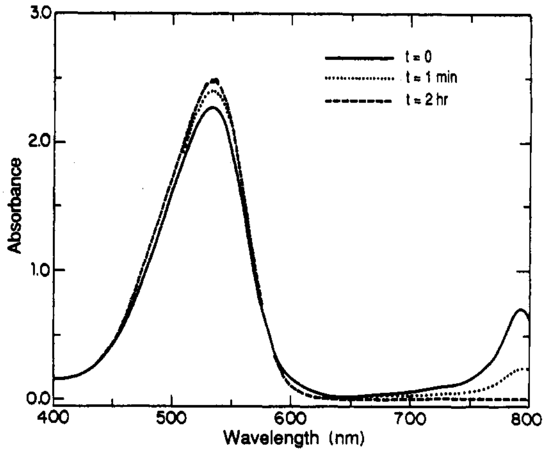


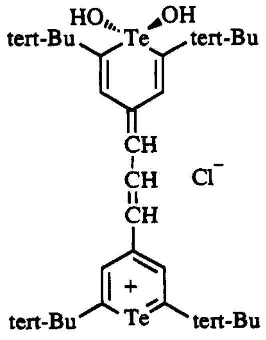
Figure 3. Effect of solvent on the equilibrium ratio of **5** and **9**. The 5-day-aged HMP solution of Figure 2 was diluted 100-fold with dichloromethane to give the observed spectra.

To test for the presence of chlorine, cyclohexene was added to the 0.015 M solution of **5** in HMP. In the presence of 0.1 M cyclohexene, *trans*-1,2-dichlorocyclohexane is formed with the disappearance of **5** and the appearance of the reduced dye **9**. Dilution of the HMP solution with dichloromethane does not regenerate dichloride **5** and suggests that the added cyclohexene has permanently removed chlorine from the equilibrium.

Conclusions

Oxidative addition of chlorine across the tellurium atom of tellurapyrylium dyes generates dichlorotellurium(IV) species.[10] The second-order rate constants for these reactions at ambient temperature are large ($\geq 1.8 \times 10^3$ mol^{-1} s^{-1} in the case of **4**), leading to synthetically useful reactions. However, at temperatures of 323 K or above in dilute solutions, reductive elimination to generate reduced tellurapyrylium dye is observed.

From kinetic studies, the reductive elimination of chlorine is first order in the dichlorotellurium(IV) compound and the rate of reductive elimination is only slightly affected by changes in solvent polarity. Mechanistically, path A of Scheme IV is consistent with these data since little charge would be developed along the reaction coordinate. For a concerted reductive elimination of chlorine, participation of the carbon π-framework would assist in cleavage of tellurium–chlorine bonds. Experimentally, the increased rate of reductive elimination with dichlorotellurium(IV) compound **19** relative to **2**–**5** and the slow rate of reductive elimination in neutral dihalotellurium(IV) compounds **16** and **17** are consistent with π-framework participation in the reductive elimination.



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Regeneration of benzenoid aromaticity lowers $\Delta H^\ddagger$ and E_a for **19** relative to **2–5** and leads to a more negative value of $\Delta S^\ddagger$ for **19** relative to **2–5**, consistent with an earlier transition state with increased π-participation for **19**.

The activation parameters calculated for the reductive elimination of chlorine from **3** and **5** are quite similar to those calculated for **1** and its ditellurium analogue **21**. For **1**, $\Delta H^\ddagger$ is 20.5 kcal mol^{-1} and $\Delta S^\ddagger$ is 11 cal mol^{-1} K^{-1} in aqueous media[7] and, for **5**, $\Delta H^\ddagger$ is 23.1 kcal mol^{-1} and $\Delta S^\ddagger$ is 12 cal mol^{-1} K^{-1} in acetonitrile and $\Delta H^\ddagger$ is 23.4 kcal mol^{-1} and $\Delta S^\ddagger$ is 13 cal mol^{-1} K^{-1} in tetrachloroethane. Similarly, for **21**, $\Delta H^\ddagger$ is 20.9 kcal mol^{-1} and $\Delta S^\ddagger$ is 11 cal mol^{-1} K^{-1} in aqueous media[7] and, for **3**, $\Delta H^\ddagger$ is 20.0 kcal mol^{-1} and $\Delta S^\ddagger$ is 4 cal mol^{-1} K^{-1} in acetonitrile and $\Delta H^\ddagger$ is 21.4 kcal mol^{-1} and $\Delta S^\ddagger$ is 7 cal mol^{-1} K^{-1} in tetrachloroethane. Since the energy barriers in the two different reductive elimination reactions are similar, similar mechanistic paths are suggested.[15]

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(15) The pH dependence cited in ref 7 for the observed rates of reaction may in fact be examples of hydroxide catalysis similar to the chloride catalysis described here.