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Sulfur and Selenium Atom Transfer Reactions of Tin Porphyrins

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Abstract: Treatment of (*meso*-tetraphenylporphyrinato)tin(IV) sulfide, (TPP)Sn=S, with (*meso*-tetra-*p*-tolylporphyrinato)tin(II), (TTP)Sn^{II}, in toluene results in the reversible exchange ($K = 1.21 \pm 0.03$ at −10 °C) of a sulfur ligand to form (TPP)Sn^{II} and (TTP)Sn=S. The net result is a formal two-electron redox process between Sn^{II} and Sn^{IV}. This occurs with a second-order rate constant at 30 °C of 0.40 ± 0.05 M^{-1} s^{-1} ($\Delta H^{\ddagger} = 10.9 \pm 0.9$ kcal/mol, $\Delta S^{\ddagger} = -24.1 \pm 2.8$ cal(mol·K)$^{-1}$). Similarly, treatment of (*meso*-tetraphenylporphyrinato)tin(IV) selenide, (TPP)Sn=Se, with (*meso*-tetra-*p*-tolylporphyrinato)tin(II), (TTP)Sn^{II}, in toluene results in the reversible exchange ($K = 1.45 \pm 0.13$ at −10 °C) of a selenium ligand to form (TPP)Sn^{II} and (TTP)Sn=Se. This reaction occurs with a second-order rate constant at 30 °C of 87.3 ± 8.06 M^{-1} s^{-1} ($\Delta H^{\ddagger}$ 9.3 ± 0.5 kcal/mol, $\Delta S^{\ddagger} = -18.8 \pm 1.5$ cal(mol·K)$^{-1}$). Discussion of an inner sphere mechanism involving a μ-sulfido or a μ-selenido bridged intermediate is presented. The rate ratio of selenium to sulfur atom transfer is 218:1 at 30 °C. This rate behavior follows the "normal" trend as observed for the analogous halogen transfer reactions ($I^- > Br^- > Cl^- > F^-$).

Atom transfer reactions continue to be an area of fundamental importance. Numerous studies have focused on oxygen atom transfer due to its relevance in both biological systems and industrial or laboratory oxidation processes.[2,3] While these have provided a large number of examples involving the transfer of an oxygen atom between a metal center and organic or nonmetal substrates, the related process of intermetal oxygen atom transfer reactions is still underdeveloped by comparison. The scope of intermetal oxygen atom transfer has recently been reviewed.[4]

Relatively few studies have been reported on sulfur or selenium atom transfer. Examples involving the transfer of a sulfur or selenium atom from a non-metal species (e.g. phosphine chalcogenides or ethylene sulfide) to a low-valent metal center have recently been utilized to prepare novel terminal sulfido and selenido complexes of the early transition metals.[5] These reactions are unusual in that phosphines generally remove sulfur from metal complexes due to the strength of the phosphine sulfide bond (≅92 kcal/mol).[6] Intermetal atom transfer reactions utilizing Cp_2TiS_5 and Cp_2TiSe_5 as chalcogen transfer reagents have provided a synthetic route to new terminal and perchalcogenido species.[7−10] These reactions formally represent a secondary atom transfer process[3a] since reduction of the η^2-X_5 (X = S, Se) ligand has taken place.[4]

Metalloporphyrin complexes have been used to investigate a variety of innersphere redox processes involving intermetal halogen,[11] oxygen,[12] and nitrogen atom transfer reactions.[13,14] We recently reported the discovery of intermetal oxygen, sulfur, and selenium atom transfer reactions involving titanium porphyrin complexes (eq 1).[15,16] Equation 1 also represents a secondary atom transfer process in which X_2^{2-} is reduced to $2X^{2-}$.[4]

$$\begin{gathered}(\mathrm{OEP})\mathrm{Ti}(\mathrm{X}_2) + (\mathrm{TTP})\mathrm{Ti}(\mathrm{PhC{\equiv}CPh}) \rightarrow \\ (\mathrm{OEP})\mathrm{Ti{=}X} + (\mathrm{TTP})\mathrm{Ti{=}X} + \mathrm{PhC{\equiv}CPh} \quad (1) \\ \mathrm{X} = \mathrm{O, S, Se}\end{gathered}$$

We now report the first comprehensive study of intermetal two-electron transfer mediated by sulfur or selenium atom transfer. The tin porphyrin complexes utilized for this work were recently described by Guilard *et al.*[9,17]

Experimental Section

Instrumentation. All synthetic procedures were performed in a Vacuum Atmospheres glovebox equipped with a Model MO40H Dri-Train gas purifier. UV−visible spectroscopic measurements were obtained on a Hewlett-Packard HP 8452A diode array spectrophotom-

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[16] Abbreviations: TTP is the *meso*-tetra-*p*-tolylporphyrinato dianion, OEP is the octaethylporphyrinato dianion, and TPP is the *meso*-tetraphenylporphyrinato dianion.

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eter. NMR spectra were recorded on a Nicolet NT300 spectrometer or on a Varian VXR 300-MHz spectrometer.

Chemicals. Toluene, tetrahydrofuran, toluene-d_8, benzene-d_6, and hexane for glovebox use were distilled from purple sodium/benzophenone ketyl solutions. Dry solvents were subsequently degassed on a vacuum line (10^{-5} Torr) with three successive freeze–pump–thaw cycles. $(\mathrm{THF})_2\mathrm{Li}_2(\mathrm{TTP})$ and $(\mathrm{THF})_2\mathrm{Li}_2(\mathrm{TPP})$ were prepared according to the literature procedure for $(\mathrm{THF})_2\mathrm{Li}_2(\mathrm{OEP})$.[18] (TTP)Sn=S and (TPP)Sn=S were prepared as described previously.[9] SnI_2, $\mathrm{Cp}_2\mathrm{TiS}_5$, and gray selenium were purchased from Aldrich and used without further purification. The following procedures are new synthetic routes for the preparation of previously reported tin porphyrins.[9,17] Spectroscopic data for the tin complexes agree with the literature values.

(TTP)Sn^{II}. SnI_2 (153 mg, 0.410 mmol) and $(\mathrm{THF})_2\mathrm{Li}_2(\mathrm{TTP})$ (144 mg, 0.174 mmol) were stirred in toluene (15 mL) at ambient temperature for 12 h, resulting in a color change from blue-green to dark green. The solution was then purified by column chromatography using a 1 × 10 cm neutral alumina column and toluene as the eluent. A green fraction containing (TTP)Sn^{II} was collected from the column and evaporated to dryness. The product was triturated in hexane (10 mL), collected by filtration, washed with hexane, and dried in vacuo (27.1 mg, 20%). (TPP)Sn^{II} was prepared in an analogous manner. (TTP)-Sn^{II}: ^{1}H NMR ($\mathrm{C_6D_6}$, ppm) 9.19 (s, 8H, β-H), 8.04 (br, 8H, $-\mathrm{C_6}H_4\mathrm{CH_3}$), 7.27 (d, 8H, $-\mathrm{C_6}H_4\mathrm{CH_3}$), 2.40 (s, 12H, $-\mathrm{C_6H_5C}H_3$); UV–vis (toluene, nm): 400, 490, 696. (TPP)Sn^{II}: ^{1}H NMR ($\mathrm{C_6D_6}$, ppm) 9.08 (s, 8H, β-H), 8.11 (m, 8H, $-\mathrm{C_6}H_5$), 7.45 (m, 12H, $-\mathrm{C_6}H_5$); UV–vis (toluene, nm) 398, 490. 696.

(TTP)Sn=Se. SnI_2 (135 mg, 0.362 mmol) and $(\mathrm{THF})_2\mathrm{Li}_2(\mathrm{TTP})$ (133 mg, 0.161 mmol) were stirred in toluene (15 mL) at ambient temperature for 12 h. The solution was then purified on a 1 × 10 cm neutral alumina column with toluene as the eluent. A green fraction containing (TTP)Sn^{II} was collected from the column. Gray selenium (19 mg, 0.23 mmol) was added to this solution and the mixture was stirred for 12 h at 50–60 °C. After the reaction mixture was filtered to remove excess selenium, the solvent was removed under reduced pressure. The product was triturated in hexane (10 mL), collected by filtration, washed with hexane, and dried in vacuo (46.2 mg, 33% based on $(\mathrm{THF})_2\mathrm{Li}_2$-(TTP)). (TPP)Sn=Se was prepared in an analogous manner. (TTP)Sn=Se: ^{1}H NMR ($\mathrm{C_6D_6}$, ppm) 9.16 (s, 8H, β-H), 7.89 (d, 8H, $-\mathrm{C_6}H_4\mathrm{CH_3}$), 7.25 (br, 8H, $-\mathrm{C_6}H_4\mathrm{CH_3}$), 2.39 (s, 12H, $-\mathrm{C_6H_4C}H_3$); UV–vis (toluene, nm) 346, 438 (Soret), 532, 570, 612. (TPP)Sn=Se: ^{1}H NMR ($\mathrm{C_6D_6}$, ppm) 9.02 (s, 8H, β-H), 7.91 (m, 8H, $-\mathrm{C_6}H_5$), 7.42 (m, 12 H, $-\mathrm{C_6}H_5$); UV–vis (toluene, nm) 344, 438 (Soret), 524, 568, 610.

Equilibrium Measurements. Samples for equilibrium determinations were prepared in a glovebox by adding specific volumes of known-concentration stock solutions of a sulfide or selenide complex, the appropriate tin(II) species, and an internal standard, triphenylmethane, into a 5-mm NMR tube attached to a ground glass joint. The solvent was removed under reduced pressure. The tube was then attached to a high-vacuum stopcock and connected to a high-vacuum line. After toluene-d_8 was added by vacuum distillation, the tube was flame sealed. The equilibrium constants were determined using a Lorentzian curve fitting to obtain an integrated intensity for each of the β-pyrrole signals associated with the species involved in the equilibrium. The samples were monitored in a temperature-controlled NMR probe until no further change in peak areas was observed.

Kinetic Measurements. The concentrations of toluene stock solutions were determined spectrophotometrically prior to use. Rate data for the (TTP)Sn^{II}/(TPP)Sn=X (X = S or Se) system were obtained on a UV–visible spectrophotometer equipped with a thermally regulated cell holder. Solutions of (TTP)Sn^{II} and (TPP)Sn=S were loaded in a 1-mm cuvette in a glovebox. Typical initial concentrations ranged from 8.2×10^{-5} to 8.0×10^{-4} M for (TTP)Sn^{II} and 3.0×10^{-4} to 7.4×10^{-4} M for (TPP)Sn=S. Initial Sn^{IV} and Sn^{II} concentrations were varied from a ratio of approximately 1:2 to 9:1. For the (TTP)Sn^{II}/(TPP)-Sn=Se system, solutions of (TTP)Sn^{II} and (TPP)Sn=Se were loaded in a 1-cm cuvette in a glovebox. Typical initial concentrations ranged from 5.61×10^{-5} to 1.70×10^{-4} M for (TTP)Sn^{II} and 1.31×10^{-5} to 3.34×10^{-5} M for (TPP)Sn=Se. Initial Sn^{IV} and Sn^{II} concentrations were varied from a ratio of approximately 1.7:1 to 13:1. For both the sulfur and selenium transfer systems, the sealed cuvette was placed in the cell holder, and the run was monitored at 612 nm. Molar absorptivities of the metalloporphyrins at 612 nm are given in Table 1. Rate constants were obtained by using an integrated rate law for second-order equilibrium reactions as derived by King.[19] The rate constants reported were determined by averaging the values obtained from three or more individual kinetic runs. Equilibrium constants for the temperatures used in the kinetic study were extrapolated from the ^{1}H NMR equilibrium data.

Table 1. Molar Absorptivities for Metalloporphyrins in Toluene at 612 nm

compd	molar absorptivity × 10^{-4} ($\mathrm{M^{-1}\,cm^{-1}}$)	compd	molar absorptivity × 10^{-4} ($\mathrm{M^{-1}\,cm^{-1}}$)
(TTP)Sn^{II}	0.232	(TTP)Sn=S	1.082
(TPP)Sn^{II}	0.316	(TPP)Sn=S	0.816
(TTP)Sn=Se	0.767	(TPP)Sn−Se	0.646

Table 2. Equilibrium Constants for Eq 2 in Toluene-d_8

temp (°C)	K
−40	1.44 ± 0.12
−30	1.37 ± 0.14
−20	1.33 ± 0.03
−10	1.21 ± 0.03

Table 3. Forward Rate Constants for Eq 2 in Toluene

temp (°C)	k_f ($\mathrm{M^{-1}\,s^{-1}}$)
30	0.40 ± 0.05
40	0.83 ± 0.12
50	1.41 ± 0.05
60	2.39 ± 0.77

Results

Reduction of Sulfidotin(IV) Porphyrin with Tin(II) Porphyrin. Treatment of (TPP)Sn=S with (TTP)Sn^{II} in toluene-d_8 results in spectral changes which are consistent with the transfer of a terminally bound sulfur ligand between two metal complexes as shown in eq 2. The use of phenyl- and tolyl-labeled porphyrins (TPP and TTP) provides a convenient means of monitoring this reaction by ^{1}H NMR. For example, new β-pyrrolic proton resonances appear, signifying the formation of (TPP)Sn^{II} (9.04 ppm) and (TTP)Sn=S (9.14 ppm). The β-pyrrolic proton signals for (TPP)Sn=S (8.99 ppm) and (TTP)-Sn^{II} (9.17 ppm) diminish but do not disappear, indicating that eq 2 is an equilibrium process. An equilibrium constant for eq 2 was measured by monitoring

$$(\mathrm{TTP})\mathrm{Sn}^{\mathrm{II}} + (\mathrm{TPP})\mathrm{Sn}{=}\mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\mathrm{TTP})\mathrm{Sn}{=}\mathrm{S} + (\mathrm{TPP})\mathrm{Sn}^{\mathrm{II}} \qquad (2)$$

the ^{1}H NMR β-pyrrole signal of each metalloporphyrin species in toluene-d_8 in flame-sealed NMR tubes. Due to the very similar nature of the porphyrins used in this study, an equilibrium constant of approximately unity was expected. As anticipated, the equilibrium constant for eq 2 in toluene-d_8 is 1.44 ± 0.12 at −40 °C and it exhibited little change over a 30 °C temperature range (K = 1.21 ± 0.03 at −10 °C). Examination of the equilibrium at higher temperatures was not possible due to overlapping of the β-pyrrole resonances of the tetratolylporphyrinato species. A summary of the equilibrium

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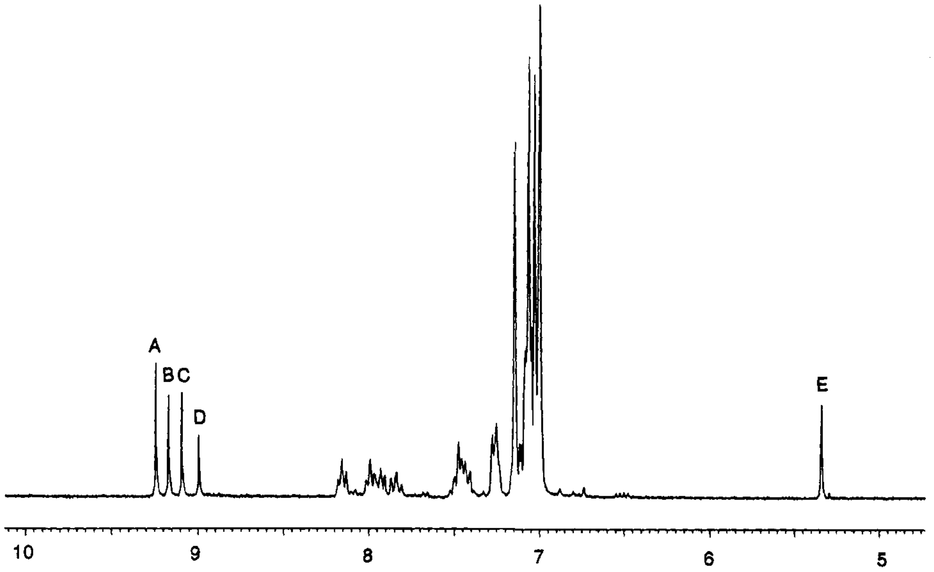

Figure 1. 300-MHz ^{1}H NMR spectrum for eq 4. A is the β-pyrrole signal for (TTP)Sn^{II}, B is the β-pyrrole signal for (TTP)Sn=Se, C is the β-pyrrole signal for (TPP)Sn^{II}, D is the β-pyrrole signal for (TPP)Sn=Se, and E is the methine signal of Ph$_3$CH.

constants for eq 2 is given in Table 2. The thermodynamic parameters, $\Delta H° = -0.66 \pm 0.13$ kcal/mol and $\Delta S° = -2.12 \pm 0.40$ cal (mol·K)$^{-1}$, were determined from this temperature dependence.

It is also possible to follow this sulfur transfer reaction using UV–vis spectroscopy. Treatment of (TPP)Sn=S with (TTP)-Sn^{II} produces spectral changes consistent with the transfer of a terminally bound sulfur ligand. For example, bands at 570 and 612 nm, which are associated with both of the terminal sulfide species, increase in intensity over the course of the reaction. These changes are in agreement with the magnitudes of the extinction coefficients for the terminal sulfide complexes. Throughout the reaction, a well-defined isosbestic point is observed at 630 nm.

The forward rates of eq 2 in toluene were examined spectrophotometrically by following the absorbance changes at 612 nm. A summary of rate constants for the forward direction is given in Table 3. In all kinetic runs, the data were found to obey an integrated rate law for reversible second-order reactions (eq 3).[19] Plots of ln[$\Delta/\alpha + \Delta(1 - 1/K)$)] vs time are linear for at least 3 half-lives.

$$\ln\left[\frac{\Delta}{\alpha + \Delta(1 + 1/K)}\right] = -\alpha k_1 t + \text{constant} \qquad (3)$$

Reduction of Selenidotin(IV) Porphyrin with Tin(II) Porphyrin. Reversible intermetal selenium atom transfer occurs on treatment of (TPP)Sn=Se with (TTP)Sn^{II} in toluene-d_8 (eq 4).

$$(\text{TTP})\text{Sn}^{\text{II}} + (\text{TPP})\text{Sn=Se} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\text{TTP})\text{Sn=Se} + (\text{TPP})\text{Sn}^{\text{II}} \qquad (4)$$

This reaction parallels the analogous sulfur atom transfer process and can also be monitored by ^{1}H NMR. For example, as shown in Figure 1, new β-pyrrolic proton resonances appear for (TPP)-Sn^{II} (9.04 ppm) and (TTP)Sn=Se (9.14 ppm) while the signals associated with the β-pyrrolic protons of (TPP)Sn=Se (8.99 ppm) and (TTP)Sn^{II} (9.17 ppm) diminish. An equilibrium constant for eq 4 was determined by ^{H} NMR by monitoring the β-pyrrole signals of the each metalloporphyrin species versus the methine proton of triphenylmethane (5.38 ppm) in toluene-d_8. As expected, the equilibrium constant for eq 4 was found to be nearly unity ($K = 1.54 \pm 0.20$ at −40 °C) and varied little over a 30 °C temperature range ($K = 1.45 \pm 0.13$ at −10 °C). Again, overlapping of the β-pyrrole resonances for the tetratolylporphyrinato species prevented studying this equilibrium at higher temperatures. A summary of the equilibrium constants for eq 4 is given in Table 4. The thermodynamic parameters, $\Delta H° = -0.25 \pm 0.02$ kcal/mol and $\Delta S° = -0.23 \pm 0.06$ cal (mol·K)$^{-1}$, were determined from this temperature dependence.

Table 4. Equilibrium Constants for Eq 4 in Toluene-d_8

temp (°C)	K
−40	1.54 ± 0.20
−30	1.51 ± 0.17
−20	1.47 ± 0.14
−10	1.45 ± 0.13

Table 5. Forward Rate Constants for Eq 4 in Toluene

temp (°C)	k_f (M^{-1} s^{-1})
0	14.4 ± 1.3
10	31.7 ± 5.1
20	59.2 ± 3.5
30	87.3 ± 8.1

The selenium atom transfer reaction depicted in eq 4 was also examined by using UV–vis spectroscopy. Treatment of (TPP)Sn=Se with (TTP)Sn^{II} in toluene results in spectral changes very similar to those observed in the transfer of a terminal sulfide ligand. Again, increases in absorbance at 570 and 612 nm were observed, consistent with the differences in extinction coefficients of the two terminal selenide complexes involved in the equilibrium. A well-defined isosbestic point was observed at 630 nm.

The forward rates of eq 4 in toluene were examined spectrophotometrically by following the absorbance changes at 612 nm. A summary of the forward rate constants for eq 4 is given in Table 5. In all kinetic runs, the data were found to obey an integrated rate law for reversible second-order reactions as shown in eq 3. Plots of ln[$\Delta/(\alpha + \Delta(1 - 1/K))$] vs time are linear for at least 3 half-lives. A typical kinetic curve and the corresponding ln plot are illustrated in Figure 2.

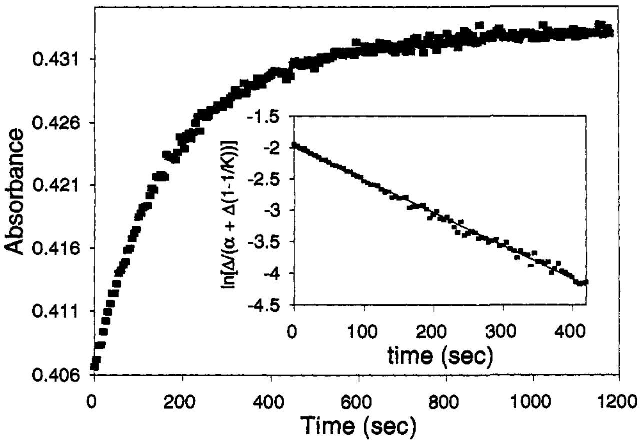

Figure 2. Representative absorption (612 nm) vs time plot for reaction 4 at 20 °C. $[(TPP)Sn{=}Se]_0 = 4.09 \times 10^{-5}$ M and $[(TTP)Sn^{II}]_0 = 4.86 \times 10^{-5}$ M. Inset: Plot of $\ln[\Delta/(\alpha + \Delta(1 - 1/K))]$ vs t.

Discussion

We have found that complete sulfur and selenium atom transfer between two metalloporphyrins can be achieved. This study represents the first comprehensive study of intermetal two-electron transfer mediated by sulfur or selenium atom transfer. It is possible to observe this process by using different porphyrin ligands as UV−vis and ^{1}H NMR spectroscopic labels. An additional benefit derived from the use of metalloporphyrins arises from the structural integrity maintained by these complexes throughout the reaction, eliminating complications due to ancillary ligand loss. Furthermore, stereochemical rearrangements found in other atom transfer systems are not possible here.[20,21] Rate constants for sulfur atom transfer (eq 2) have been measured over a 30 °C temperature span. These rate constants range between 0.40 and 2.39 $M^{-1}\,s^{-1}$ for the forward direction. Varying the ratio of initial concentrations of Sn^{IV} to Sn^{II} from 1:2 to 9:1 resulted in comparable rate constants within experimental error, indicating a reaction that is first order in each of the starting components. The temperature dependence of the forward rate yields activation parameters of $\Delta H^{\ddagger} = 10.9 \pm 0.9$ kcal/mol and $\Delta S^{\ddagger} = -24.1 \pm 2.8$ cal (mol•K)$^{-1}$. In an analogous manner, selenium atom transfer rate constants were measured over a 30 °C temperature range. The forward rate constants range between 14.4 and 87.3 $M^{-1}\,s^{-1}$. Varying the ratio of initial concentrations of Sn^{II} and Sn^{IV} from 1.7:1 to 13:1 resulted in comparable rate constants within experimental error, indicating a reaction that is first order in each of the starting components. In this case, the temperature dependence of the forward rate yields activation parameters of $\Delta H^{\ddagger} = 9.3 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -18.8 \pm 1.5$ cal (mol•K)$^{-1}$. Since $\Delta G° \approx 0$, the activation parameters for eq 2 and 4 reflect the intrinsic tendency for sulfur or selenium atom transfer, respectively.

Electrochemical studies on tin porphyrins suggest that eqs 2 and 4 do not involve an outersphere mechanism.[17,22] Kadish *et al.* have demonstrated that the first and second electrochemical reductions of (TTP)Sn=S and (TTP)Sn=Se are ligand-based. Formation of the singly reduced complexes occurs at $E_{1/2} = -0.88$ V ((TTP)Sn=S) and $E_{1/2} = -0.87$ V ((TTP)Sn=Se) vs SCE. Since the $[(TTP^{-})Sn^{II}]^{+}/[(TTP^{2-})Sn^{II}]$ reduction potential is −0.60 V vs SCE, tin(II) porphyrins are not thermodynamically capable of reducing (POR)Sn=S or (POR)Sn=Se (POR = TTP, TPP) in an electron transfer pathway.[22]

The activation parameters for eqs 2 and 4 support an inner-sphere process. The low $\Delta H^{\ddagger}$ values suggest that significant bond formation occurs ($Sn^{IV}{=}X \cdot\cdot Sn$) to offset $Sn^{IV}{-}X$ bond dissociation. In addition, the negative entropies of activation ($\Delta S^{\ddagger} = -24.1 \pm 2.8$ cal (mol•K)$^{-1}$ for sulfur atom transfer; $\Delta S^{\ddagger} = -18.8 \pm 1.5$ cal (mol•K)$^{-1}$ for selenium atom transfer) are consistent with an associative type mechanism in which atom transfer occurs via a μ-sulfido or a μ-selenido intermediate. However, we have not detected this bridged species spectroscopically by UV−vis, ^{77}Se NMR, or EPR.

Finally, the increase in rate of selenium atom transfer versus sulfur atom transfer supports the results of a previous study of atom transfer reactions involving phosphines and phosphine chalcogenides (eq 5).[23] For these reactions, it was found that

$$Ph_3P{=}X + Ph_2MeP \rightleftharpoons Ph_3P + Ph_2MeP{=}X \qquad (5)$$

$$X = O, S, Se$$

the atom transfer rate increased qualitatively with the size of the chalcogenide. However, absolute rates were not reported. The overall increase in rate in eq 5 upon descending the chalcogenide family was rationalized on the basis of diminishing covalent bond energies on progressing to the heavier elements of group 16. This can be considered the "normal" trend as observed for halide transfer.[24] The relative rate of selenium versus sulfur atom transfer in the tin process (218:1 at 30 °C) is unexpectedly large compared to systems involving halogen transfer. In a study involving halogen exchange between cobalt porphyrins, the observed rates at 298 K ($k_{Cl} = 27.1 \times 10^3\ M^{-1}\,s^{-1}$; $k_{Br} = 373 \times 10^3\ M^{-1}\,s^{-1}$; $k_I = 8170 \times 10^3\ M^{-1}\,s^{-1}$) reflect only approximately a 14-fold and 22-fold increase in rate in moving from chloride to bromide and bromide to iodide, respectively.[11a] Based on the similar size increase when substituting chloride for bromide and sulfide for selenide, an approximate 20-fold increase in relative rate was expected in the chalcogenide transfer reactions. The observed 218-fold increase in rate for selenium versus sulfur transfer may suggest a significant difference in M=S and M=Se covalent bond strengths. This supports the general premise that $p\pi{-}p\pi$ bond strengths decrease on descending the main group elements.[25] A recent illustration of this trend involves the synthesis of the heavier chalcogenide tin complexes of the macrocyclic octamethyldibenzotetraaza[14]annulene ligand.[26] While the terminal sulfido and selenido complexes were readily isolated, the terminal tellurido species could not be isolated, suggesting a weak Sn=Te interaction.

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