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Kinetic Study of the Two-Electron Oxidation of Cobalt Tetraneopentoxyphthalocyanine by Thionyl Chloride

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Electronic spectroscopy was used to study the kinetics of the reaction between $Co^{II}TnPc(2-)$ and $SOCl_2$ in 1,2-dichlorobenzene. $SOCl_2$ reacts rapidly with $Co^{II}TnPc(2-)$ to yield the two-electron-oxidized species $Cl_2Co^{III}TnPc(1-)$ and a $(SOCl_2)Co^{II}TnPc(2-)$ adduct; estimates of the rate constants for formation of these species are derived from stopped-flow data. The adduct further reacts with another molecule of $SOCl_2$ ($k_4 = 1.51 \pm 0.50$ $M^{-1}\ s^{-1}$ at 22.2 °C, $\Delta H^{\ddagger} = 13.5 \pm 1.1$ kcal/mol, $\Delta S^{\ddagger} = -11.9 \pm 3.3$ cal/(mol deg) to yield $Cl_2Co^{III}TnPc(1-)$. In the presence of HCl, oxidation to form only $Cl_2Co^{III}TnPc$ proceeds very slowly. Implications for Li/$SOCl_2$ batteries are discussed.

Introduction

Cobalt phthalocyanine (CoPc) plays an important role in lithium/thionyl chloride ($SOCl_2$) batteries (the highest energy density system known to date[1]). Addition of CoPc to a Li/$SOCl_2$ cell improves the voltage, current, and lifetime of the cell.[2−9] We have previously shown[10] that a catalytic two-electron mechanism is indicated for the reduction of thionyl chloride in a Li/$SOCl_2$/(CoTnPc,C) battery. This two-electron reduction process could result in a safer Li/$SOCl_2$ battery by eliminating reactive intermediates that may form when $SOCl_2$ is reduced by one electron at a carbon cathode not treated with cobalt phthalocyanine.

In this paper we present the kinetics of the two-electron reaction between $Co^{II}TnPc(2-)$ and $SOCl_2$. The kinetics were studied to obtain mechanistic information about this important and interesting reaction.

Experimental Section

Cobalt tetraneopentoxyphthalocyanine (abbreviated CoTnPc) used because of its high solubility in organic solvents, was prepared by the method of Leznoff and co-workers.[11] Nitrogen (dried over Drierite) was bubbled through thionyl chloride (reagent grade, BDH) for 5 h prior to use to remove all traces of HCl, SO_2, and dissolved oxygen. The solvent 1,2-dichlorobenzene (DCB) (Gold Label, Aldrich) was dried over 4 Å molecular sieves (8−12 mesh, Aldrich) activated at 200 °C under vacuum for 2 h. A solution of HCl in DCB was prepared by adding concentrated H_2SO_4 to concentrated HCl, passing the HCl gas through a tube containing Drierite, and then bubbling the dry HCl through DCB for 20 min.

The reaction between CoTnPc and $SOCl_2$ was followed via electronic spectroscopy using a Guided Wave Inc. Model 100-20 optical waveguide spectrum analyzer, a caliper fiber optic probe, and a 0.100 or 0.200 cm quartz cell. In a typical experiment, a 1 μL amount of dilute $SOCl_2$ (diluted 40 times in DCB) was added to a 1 mL DCB solution of CoTnPc (10^{-4} M) under nitrogen. Quickly, after the addition of $SOCl_2$ (in under 10 s), the reaction was mixed well and timed. The absorbances at selected wavelengths were subsequently measured every minute over a period of about 30 min. Extremely dry conditions were used to prevent the hydrolysis of $SOCl_2$,[12] which would lead to protonation of the phthalocyanine[13] by the HCl produced.

Stopped-flow experiments were performed under nitrogen using a Hi-Tech Scientific Shu SFh51 stopped-flow apparatus and a Hi-Tech Scientific SU40 spectrophotometer unit. The concentration of $Co^{II}TnPc(2-)$ was held constant at 6.60×10^{-6} M in DCB, and the [$SOCl_2$] was varied. Absorbance measurements were taken at 540 and 686 nm as a function of time; a typical data set is shown in Figure 1. For each concentration of $SOCl_2$, five duplicate runs were performed and the results averaged. The stopped-flow experiments were duplicated on different days using different solutions.

Extinction coefficients used in this study (λ, nm (ϵ, $M^{-1}\ cm^{-1}$): $Co^{II}TnPc(2-)$ 540 (5880), 680 (13 500), 686 (122 000); $Cl_2Co^{III}TnPc(1-)$ 540 (29 000), 680 (19 100), 686 (19 200); $ClCo^{II}TnPc(2-)\cdot H^+$ 540 (5590), 680 (42 200), 686 (45 500). Conditions: [$Co^{II}TnPc(2-)$] = 5.85×10^{-5} M, [HCl] = 0.055 M. The extinction coefficients for $Co^{II}TnPc(2-)$ are for mononuclear $Co^{II}TNPc(2-)$ in DCB[14] and differ from those reported[10] for aggregated $Co^{II}TnPc(2-)$ in DCB. At concentrations of $Co^{II}TnPc(2-)$ below 2×10^{-5} M (the conditions of the kinetic experiments (see text)), $Co^{II}TnPc(2-)$ exists as a monomeric species in solution.[14]

Results and Discussion

Introduction. Previous work[10] has shown that $Co^{II}TnPc(2-)$ upon addition of $SOCl_2$, even under substoichiometric conditions, can be rapidly oxidized by $SOCl_2$ to $Cl_2Co^{III}TnPc(1-)$, but in a parallel reaction rapidly forms a mono(thionyl chloride) adduct. Furthermore the adduct is slowly, irreversibly oxidized by two electrons also to $Cl_2Co^{III}TnPc(1-)$, which contains a radical Pc ring, two trans Co^{III}−Cl bonds, and a six-coordinate octahedral structure about the Co^{III} metal center.[15] (See ref 15 for phthalocyanine nomenclature.)

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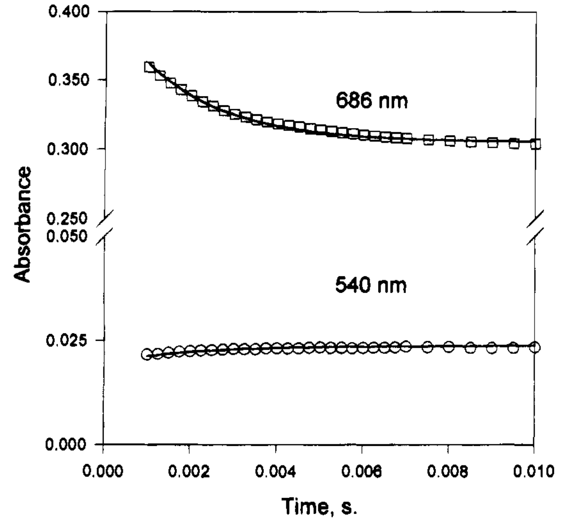

Figure 1. Stopped-flow run of $\mathrm{Co^{II}TnPc(2-)} + \mathrm{SOCl_2}$ in DCB, under $\mathrm{N_2}$, HCl-free conditions, T = 24.0 ± 0.1 °C, $[\mathrm{Co^{II}TnPc(2-)}] = 6.60 \times 10^{-6}$ M, $[\mathrm{SOCl_2}] = 2.76 \times 10^{-2}$ M; absorbance data at 540 and 686 nm as noted. The solid lines were calculated using $k_1 = 1800$, $k_2 = 17\,700$ $\mathrm{M^{-1}\,s^{-1}}$, $\epsilon(\text{adduct},540) = 5000$, $\epsilon(\text{adduct},686) = 100\,000$ $\mathrm{M^{-1}\,cm^{-1}}$, and the initial concentrations of $\mathrm{Co^{II}TnPc(2-)}$ and $\mathrm{SOCl_2}$.

Rate Expressions. The species $\mathrm{Co^{II}TnPc(2-)}$, $\mathrm{(SOCl_2)Co^{II}TnPc(2-)}$, and $\mathrm{Cl_2Co^{III}TnPc(1-)}$ absorb most strongly at 680, 686, and 540 nm, respectively (Experimental Section).[10] When $\mathrm{SOCl_2}$ (HCl free) is added to a solution of $\mathrm{Co^{II}TnPc(2-)}$ in DCB, at room temperature, there is a rapid depletion of $\mathrm{Co^{II}TnPc(2-)}$ to yield $\mathrm{(SOCl_2)Co^{II}TnPc(2-)}$ and $\mathrm{Cl_2Co^{III}TnPc(1-)}$ (as indicated by electronic spectroscopy), occurring upon mixing, in a time span of less than 1 s.

$$\mathrm{Co^{II}TnPc(2-) + SOCl_2 \xrightarrow{k_1} Cl_2Co^{III}TnPc(1-) + ``SO"} \tag{1}$$

$$\mathrm{Co^{II}TnPc(2-) + SOCl_2 \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} (SOCl_2)Co^{II}TnPc(2-)} \tag{2}$$

"SO" represents the initial two-electron-reduction product of $\mathrm{SOCl_2}$ but is likely to react further. XPS studies[16] suggest a dismutation of SO into sulfur and a more oxidized sulfur species. The sulfur probably results from the disproportionation reaction of SO to yield S and $\mathrm{SO_2}$.[1,17-19] Riga[16] also reports that sulfur and chloride ions are products of thionyl chloride reduction by iron and molybdenum phthalocyanines.

Fast Initial Process. The stopped-flow technique (Figure 1) was used to study the fast conversion of $\mathrm{Co^{II}TnPc(2-)}$ to $\mathrm{(SOCl_2)Co^{II}TnPc(2-)}$ and $\mathrm{Cl_2Co^{III}TnPc(1-)}$.

The appropriate rate expression, assuming k_{-2} is negligible,[20] may be written

$$[\mathrm{Co^{II}}]_t = [\mathrm{Co^{II}}]_0 e^{-(k_1+k_2)[\mathrm{SOCl_2}]t} \tag{3}$$

where $[\mathrm{Co^{II}}]_t$ and $[\mathrm{Co^{II}}]_0$ represent the concentrations of starting material $\mathrm{Co^{II}TnPc(2-)}$ at times t and time zero, respectively. The concentrations of the two products then follow

$$[\mathrm{Co^{III}}]_t = \{[\mathrm{Co^{II}}]_0 - [\mathrm{Co^{II}}]\}_t k_1/(k_1 + k_2) \tag{4}$$

and the concentration of the adduct from

$$[\text{adduct}]_t = \{[\mathrm{Co^{II}}]_0 - [\mathrm{Co^{II}}]\}_t k_2/(k_1 + k_2) \tag{5}$$

It is also obviously true that the sum of the three components at any time is equal to the initial concentration of $\mathrm{Co^{II}TnPc(2-)}$.

Without knowledge of the extinction coefficients of the adduct at the relevant wavelengths, or estimated values therefore, it is impossible to extract individual values of k_1 and k_2; only their sum can be extracted from the data.

The absorbance at any given wavelength may be written

$$A(\lambda)_t = [\mathrm{Co^{II}}]_t\epsilon(\mathrm{Co^{II}},\lambda) + [\mathrm{Co^{III}Pc}]_t\epsilon(\mathrm{Co^{III}},\lambda) + [\text{adduct}]_t\epsilon(\text{adduct},\lambda) \tag{6}$$

where $\epsilon(\mathrm{Co^{II}},\lambda)$, $\epsilon(\mathrm{Co^{III}},\lambda)$, and $\epsilon(\text{adduct},\lambda)$ are the molar absorbances of the reactant and two products at wavelength λ. The stopped-flow data at 540 and 686 nm were solved for the sum $(k_1 + k_2)$ using the Curve Fit program in Sigmaplot[21] based upon eqs 3–6. Mean values of $(k_1 + k_2)$ were obtained from four independent stopped-flow experiments, with three giving similar results but one giving a significantly larger result. Application of the T_n statistical test allowed the high value to be excluded at the 99% confidence level. The average value for $(k_1 + k_2)$ from three multiple-run (see Experimental Section) stopped-flow experiments is 18 140 $\mathrm{M^{-1}\,s^{-1}}$ with a standard deviation of 1480 $\mathrm{M^{-1}\,s^{-1}}$.

Although the extinction coefficients of the adduct at 540 and 686 nm are unavailable, it is possible to estimate limits for the value at 540 nm from the well-known spectroscopic behavior of $\mathrm{LCo^{II}Pc}$ species.[22,23] It is safe to presume that the molecular extinction coefficient of the adduct at 540 nm, $\epsilon(\text{adduct},540)$, will be very small. If we make the limiting assumption that the extinction coefficient lies between 0 and 5000 $\mathrm{M^{-1}\,cm^{-1}}$, k_1 lies in the range $(2.1(\pm0.2)-5.0(\pm0.5)) \times 10^3$ $\mathrm{M^{-1}\,s^{-1}}$ and k_2 in the range $(1.3(\pm0.1)-1.6(\pm0.15)) \times 10^4$ $\mathrm{M^{-1}\,s^{-1}}$, averaging data from the three stopped-flow experiments. It is not possible to make any accurate presumptions about $\epsilon(\text{adduct},686)$.

Slow Subsequent Process. After about 1 s, the principal chemistry is the slow conversion of the adduct into $\mathrm{Cl_2Co^{III}TnPc(1-)}$, a process which could theoretically occur by three possible pathways. Oxidation could occur via a first-order mechanism (reaction 7), via a second-order mechanism (reaction 8), or via loss of $\mathrm{SOCl_2}$ (k_{-2}) followed by reaction 1.

$$\mathrm{(SOCl_2)Co^{II}TnPc(2-) \xrightarrow{k_3} Cl_2Co^{III}TnPc(1-) + ``SO"} \tag{7}$$

$$\mathrm{(SOCl_2)Co^{II}TnPc(2-) + SOCl_2 \xrightarrow{k_4} Cl_2Co^{III}TnPc(1-) + ``SO" + SOCl_2} \tag{8}$$

For the slower oxidation of the adduct, one can assume that $d[\mathrm{Co^{II}TnPc(2-)}]/dt \approx 0$, since beyond 1 s into the experiment

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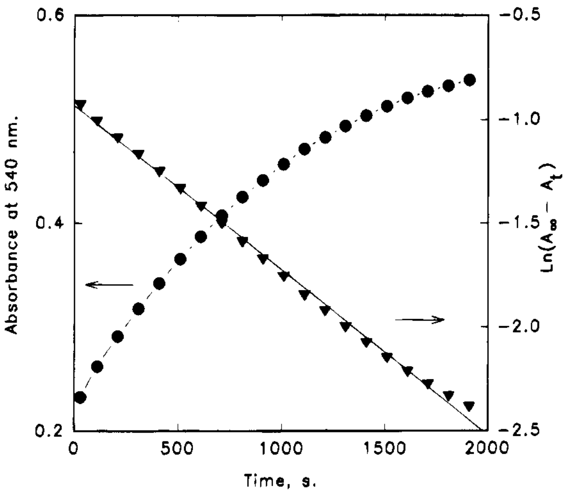

Figure 2. Long-time growth of the absorbance at 540 nm versus time: plot showing raw absorbance data (left-hand axis); plot of ln [$A_\infty - A_t$] vs time (right-hand axis). [CoTnPC(2−)] = 1.03 × 10^{-4} M, [SOCl$_2$] = 6.6 × 10^{-4} M. Path length = 0.2 cm.

there is no significant concentration of Co^{II}TnPc(2−) left.[24] Hence, one can derive, without making the assumption that equilibrium holds for reaction 2[25]

$$-\mathrm{d}[\text{adduct}]/\mathrm{d}t = (k_1k_{-2}/(k_1 + k_2) + k_3 + k_4[\mathrm{SOCl_2}])[\text{adduct}] \quad (9)$$

Three terms appear in the rate expression arising from the three pathways in which the adduct can be oxidized by Cl$_2$-Co^{III}TnPc(1−). Using classical kinetic methods (following spectroscopic changes using the Guided Wave spectrometer), the slow subsequent oxidation of the adduct to Cl$_2$Co^{III}TnPc(1−) was followed as a function of time (Figure 2), following the growth of the absorbance at 540 nm which is primarily due to the Cl$_2$Co^{III}TnPc(1−) species. A conventional plot of ln [$A_\infty - A_t$] versus t yields[26] a value for k_{obs} where

$$k_{\mathrm{Obs}} = k_1k_{-2}/(k_1 + k_2) + k_3 + k_4[\mathrm{SOCl_2}] \quad (10)$$

In principle, the same data can be extracted from analysis of the absorbance at 680 and 686 nm versus time. In practice, over the length of time of the experiment, it is very difficult to prevent some trace contamination of water which, via reaction with SOCl$_2$, generates HCl, which then reacts with the adduct to form Co^{II}TnPc(2−)·HCl (vide infra). Consideration of the relevant spectroscopic data (see Experimental Section) shows that trace quantities of this species will have a much larger effect upon the observed absorbances at 680 and 686 nm than they will at 540 nm, rendering analysis at these wavelengths less reliable.

While k_{obs} for the oxidation of the adduct, as required by the rate expression, showed no dependence upon the concentration of CoTnPc,[2]17 it does, on the other hand, vary linearly with the concentration of SOCl$_2$ (Table 1, Figure 3A). The slope of this correlation yields a value of k_4 = 1.51 ± 0.50 M^{-1} s^{-1} at room temperature. Figure 3B,C reveals what happens at low concentrations of SOCl$_2$ wherein k_{obs} was plotted against the concentration of SOCl$_2$ added (Figure 3B) and against [SOCl$_2$](free) (Figure 3C). The [SOCl$_2$](free) is defined as the concentration of SOCl$_2$ added minus the concentration of CoTnPc. This accounts for the loss of 1 equiv of SOCl$_2$ at the start of the reaction when all of the Co^{II}TnPc(2−) is converted either to the adduct or to Cl$_2$Co^{III}TnPc(1−) and represents the amount of free SOCl$_2$ that can react, actually present in solution.

Table 1. Kinetic Data for the Oxidation of (SOCl$_2$)Co^{II}TnPc(2−) by SOCl$_2$ (HCl Free) in DCB under N$_2$, as a Function of the Concentration of SOCl$_2$ and Temperature

[SOCl$_2$] (M)	[CoTnPc] (M × 10^{-4})	[SOCl$_2$](free) (M)	T (°C)	k_{obs} (s^{-1})
		T ± 0.1 °C		
6.89 × 10^{-5}	1.29	0	23.3	0
7.92 × 10^{-5}	1.33	0	22.5	0.0000037
1.11 × 10^{-4}	1.06	5 × 10^{-6}	22.9	0.000117
1.34 × 10^{-4}	1.29	5 × 10^{-6}	23.2	0.000104
1.45 × 10^{-4}	1.33	1.2 × 10^{-5}	22.5	0.000140
2.59 × 10^{-4}	1.00	1.59 × 10^{-4}	22.9	0.000400
2.81 × 10^{-4}	1.33	1.48 × 10^{-4}	22.5	0.000392
4.40 × 10^{-4}	1.05	3.35 × 10^{-4}	22.9	0.000547
6.60 × 10^{-4}	1.03	5.57 × 10^{-4}	22.9	0.00102
9.16 × 10^{-4}	1.00	8.16 × 10^{-4}	22.9	0.00155
1.38 × 10^{-3}	1.23	1.26 × 10^{-3}	21.1	0.00219
1.71 × 10^{-3}	1.50	1.56 × 10^{-3}	21.2	0.00427
1.71 × 10^{-3}	1.32	1.58 × 10^{-3}	21.5	0.00223
3.03 × 10^{-3}	1.23	2.91 × 10^{-3}	21.1	0.00542
3.10 × 10^{-3}	1.25	2.98 × 10^{-3}	22.8	0.00555
3.41 × 10^{-3}	1.51	3.26 × 10^{-3}	21.2	0.00444
3.41 × 10^{-3}	1.32	3.28 × 10^{-3}	21.5	0.00471
5.51 × 10^{-3}	1.23	5.39 × 10^{-3}	21.1	0.00801
8.07 × 10^{-3}	1.32	7.94 × 10^{-3}	21.1	0.0129
1.21 × 10^{-2}	1.25	1.20 × 10^{-2}	22.8	0.0177
1.33 × 10^{-2}				0.0191[27]
2.14 × 10^{-2}	1.46	2.13 × 10^{-2}	22.8	0.0324
2.38 × 10^{-2}	1.27	2.37 × 10^{-2}	22.8	0.0367
		T ± 0.3 °C		
3.44 × 10^{-4}	1.25	2.19 × 10^{-4}	1.8	0.000078
1.71 × 10^{-3}	1.25	1.59 × 10^{-3}	1.8	0.000346
1.72 × 10^{-3}	1.40	1.58 × 10^{-3}	1.8	0.000450
3.41 × 10^{-3}	1.36	3.27 × 10^{-3}	1.8	0.000839
		T ± 0.5 °C		
3.44 × 10^{-4}	1.10	2.34 × 10^{-4}	51.6	0.00300
6.88 × 10^{-4}	1.10	5.78 × 10^{-4}	51.6	0.00827
1.01 × 10^{-3}	1.10	9.00 × 10^{-4}	51.6	0.0144
1.37 × 10^{-3}	1.10	1.26 × 10^{-3}	51.6	0.0175

When k_{obs} is plotted against low concentrations of SOCl$_2$ (Figure 3B,C), an intercept is observed (low concentrations were used to obtain an accurate value for the intercept). The x intercept in Figure 3B corresponds to the addition of 1 equivalent of SOCl$_2$ (1 × 10^{-4} M), providing further evidence that the adduct contains only one SOCl$_2$ molecule.[10]

As can be seen in Table 1, k_{obs} decreases dramatically when less than 1 equiv of SOCl$_2$ is added to a solution of Co^{II}TnPc(2−) in DCB since the k_4 pathway is "switched off".

Further information can be obtained by plotting k_{obs} vs [SOCl$_2$](free) (Figure 3C). The y intercept, in this case, yields a value of (9.9 ± 6.1) × 10^{-5} s^{-1} for $k_1k_{-2}/(k_1 + k_2) + k_3$. Since both terms must be less than or equal to the intercept value, $k_3 \le 1.6 \times 10^{-4}$ s^{-1}, $k_{-2} \le 1.7 \times 10^{-3}$ s^{-1}, and K =

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(24) This follows from evaluation of reaction 3 using the known sum k_1 + k_2.

(25) One cannot use the equilibrium constant K = [adduct]/[Co^{II}TnPc(2−)][SOCl$_2$] in the calculation of a rate law, because k_2[Co^{II}TnPc(2−)][SOCl$_2$] would then equal k_{-2}[adduct] and d[adduct]/dt would, therefore, be equal to zero.

(26) In all three possible ways in which (SOCl$_2$)Co^{II}TnPc(2−) can be oxidized to Cl$_2$Co^{III}TnPc(1−), there is no net change in the concentration of SOCl$_2$. Each molecule of (SOCl$_2$)Co^{II}TnPc(2−) which oxidizes to Cl$_2$Co^{III}TnPc(1−) uses up one molecule of SOCl$_2$ but also frees one molecule of SOCl$_2$ which was bound to Co^{II}TnPc(2−) (reaction 8). As a result of this, plots of ln [$A_\infty - A_t$] vs time (as in Figure 2) were linear even at very low concentrations of SOCl$_2$ (1 and 2 equiv).

(27) For [Co^{II}TnPc(2−)] varied from 1.93 × 10^{-5} to 6.57 × 10^{-4} M in DCB under nitrogen, the average value of k_{obs} was 0.019 ± 0.003 s^{-1} at 22.9 ± 0.2 °C for [SOCl$_2$] = 1.33 × 10^{-2} M (HCl free).

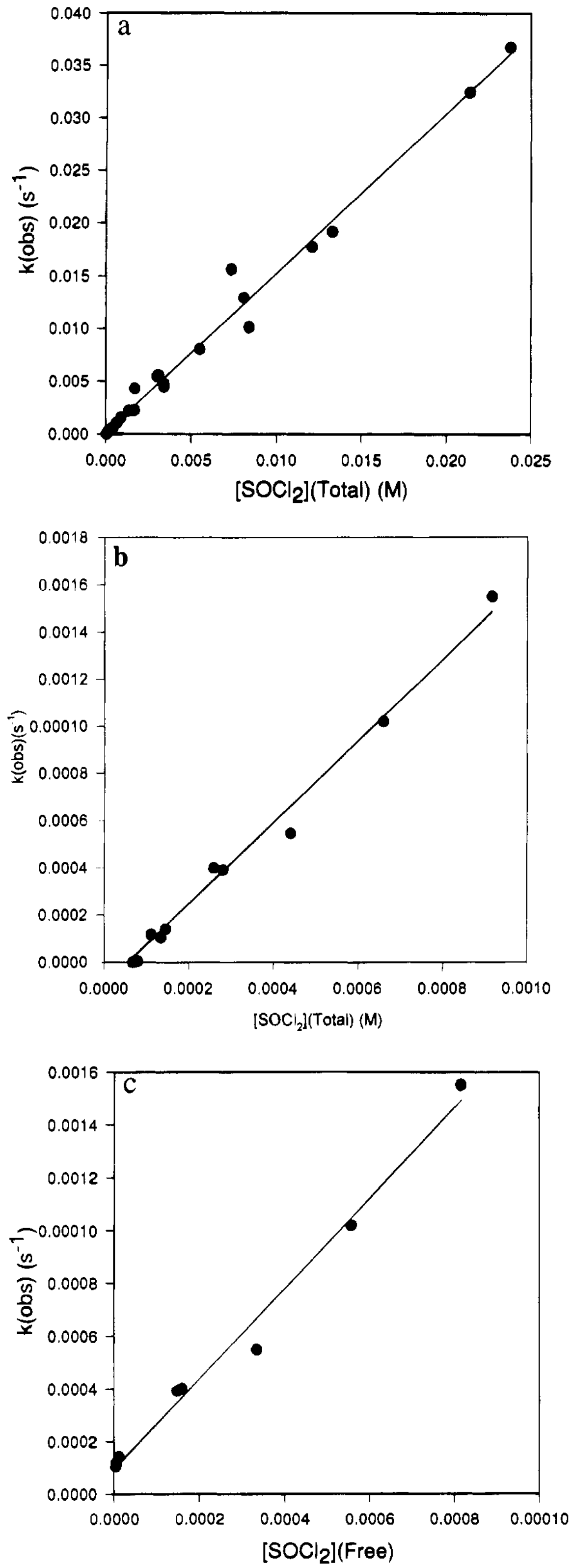

Figure 3. Data and conditions shown in Table 1: (A) variation of k_{obs} with [$SOCl_2$](total)—over a wide range of [$SOCl_2$]; (b) variation of k_{obs} with [$SOCl_2$](total) over a low concentration range of [$SOCl_2$]; (c) variation of k_{obs} with [$SOCl_2$](free) over a low concentration range of [$SOCl_2$]. See text for definition of [$SOCl_2$](free).

$k_2/k_{-2} \geq 7 \times 10^6\ M^{-1}$ (using the stopped-flow estimated limiting values for k_1 and k_2).

Mechanism. In the first fraction of a second there are two rapid processes (k_1 and k_2) in which $Co^{II}TnPc(2-)$ is consumed by $SOCl_2$ (*HCl free*) leading to different products. This is an unusual observation. In less than a second (with fairly large excess $SOCl_2$), $Co^{II}TnPc(2-)$ is converted either to the $(SOCl_2)Co^{II}TnPc(2-)$ adduct or to $Cl_2Co^{III}TnPc(1-)$ and the concentration of free $Co^{II}TnPc(2-)$ is equal to zero, within experimental error.

$SOCl_2$ can coordinate to the Co^{II} metal center through either the oxygen or sulfur atom[28] in the $(SOCl_2)Co^{II}TnPc(2-)$ adduct. Calderazzo et al.[29,30] have prepared a similar molecule. Namely, the bis adduct $(DMSO)_2FePc$ which was found, using X-ray crystallography, to contain S-bonded DMSO. Sulfuryl chloride (SO_2Cl_2) cannot bind to $Co^{II}TnPc(2-)$ through the sulfur atom. When SO_2Cl_2 is added to $Co^{II}TnPc(2-)$, the cobalt phthalocyanine is oxidized immediately (less than 1 s) to $Cl_2Co^{III}TnPc(1-)$ without the observed formation of a $(SO_2Cl_2)Co^{II}TnPc(2-)$ adduct.

This suggests that, in the solvent cage, binding of $SOCl_2$ to CoTnPc can occur via oxygen or sulfur, with the former leading rapidly to oxidation to $Cl_2Co^{III}TnPc(1-)$, while the latter forms the fairly stable adduct $(SOCl_2)Co^{II}TnPc(2-)$, which is eventually oxidized by another molecule of $SOCl_2$ (reaction 8), at a rate much slower than that of reaction 1. The large difference in the rates may be due to the fact that although $(SOCl_2)Co^{II}TnPc(2-)$ has a vacant coordination site on the cobalt center, five-coordinated Co(II) species are very stable and resistant to binding a sixth ligand.[31-34]

In the proposed formation of the transition-state complex

$$(SOCl_2\text{-}S)Co^{II}TnPc(2-) + SOCl_2 \leftrightarrow (SOCl_2)_2Co^{II}TnPc(2-) \quad (11)$$

the second molecule of $SOCl_2$ can bind to the Co(II) center via the S, Cl, or O atom. All six-coordinate $L_2Co^{II}TnPc(2-)$ configurations would favor the formation of $Co^{III}TnPc$ by raising the energy of the d_{z^2} orbital of the metal.[35]

There are not many systems known where the original reactants either generate product very rapidly or, instead, form an adduct which is many orders of magnitude less reactive. Rosenhein et al.[36] have reported a similar situation involving the oxidation of $[Co^{II}(EDTA)]^{2-}$ by $[Fe^{III}(CN)_6]^{3-}$. Electron transfer occurs via an outer sphere mechanism. The binuclear complex $[(EDTA)CoNCFe(CN)_5]^{5-}$ (inner sphere mechanism) also forms but results in a dead end pathway.

Dependence of k_4 on Temperature. Data were collected at 1.8 ± 0.3 and 51.6 ± 0.5 °C, showing a significant temperature effect on the rate constant k_4. Specifically (T, k_{obs}): 51.6 ± 0.5, 14.51 ± 0.93; 22.2 ± 0.6, 1.55 ± 0.50; 1.8 ± 0.3, 0.28 ± 0.05.

The activation parameters for reaction 8 were obtained by plotting ln (k_4/T) vs $1/T$, yielding $\Delta H^{\ddagger} = 13.5 \pm 1.1$ kcal/mol and $\Delta S^{\ddagger} = -11.9 \pm 3.3$ cal/(mol deg) and hence $\Delta G^{\ddagger}(293\ K) = 17.0 \pm 2.1$ kcal/mol. Furthermore, the fact that the Eyring

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plot is linear implies that there is no change in mechanism over the temperature range studied (2−52 °C).[37]

For the reduction of $SOCl_2$ at a platinum electrode, an overpotential of ≥ 0.51 V (depends upon the concentration of $SOCl_2$)[1] is required.[10] This overpotential corresponds to an activation energy barrier of at least 23.5 kcal/mol. Hence, at room temperature, the activation energy for the reduction of $SOCl_2$ is ca. 6.5 kcal/mol less using $Co^{II}TnPc(2-)$ than at a Pt surface, consistent with the reported shifts of 100−300 mV of the $SOCl_2$ reduction peak toward more positive potentials upon addition of CoPc to an electrochemical cell.[6,38,39]

Kinetic Studies in the Presence of HCl. Thionyl chloride readily hydrolyzes to yield HCl and SO_2.[12] The maximum solubility of HCl in thionyl chloride at room temperature is 0.28 M.[12] Brønsted acids protonate phthalocyanines, with the protons likely binding to the outer nitrogen atoms of the Pc ring.[13,40−44] In this work, the effect of the HCl on the reaction between $Co^{II}TnPc(2-)$ and $SOCl_2$ was briefly studied.

CoTnPc species can bind one or more protons depending upon the concentration of HCl.[13] These protonated species could further complicate the oxidation of cobalt phthalocyanine by $SOCl_2$.

Two runs (not shown) were performed in DCB containing HCl, using the same inert conditions as stated above. Under these conditions, the reactant is $Co^{II}TnPc(2-)\cdot HCl$. No adduct with $SOCl_2$ is formed and the rate of oxidation, k_{obs}, is some 100 times slower than for $(SOCl_2)Co^{II}TnPc$.

This observation has important implications for $Li/SOCl_2$ batteries in which CoPc is used as a catalyst. Many studies have been carried out to improve the discharge rate capability of $Li/SOCl_2$ cells.[2−5,38,39,45−53] This work predicts that if careful measures were taken to remove virtually all of the HCl from a $Li/SOCl_2$ battery containing CoTnPc (this includes the electrolyte $LiAlCl_4$ which is commonly used), then the current that could be drawn from the cell would dramatically increase.[54] We were not able to find any studies in the literature of the effect of HCl content in $Li/SOCl_2/(CoPc,C)$ cells.

Conclusions. Thionyl chloride reacts rapidly with bare $Co^{II}TnPc(2-)$ to produce the two-electron-oxidized species $Cl_2Co^{III}TnPc(1-)$ (reaction 1) and a $(SOCl_2)Co^{II}TnPc(2-)$ adduct (reaction 2). The adduct further undergoes oxidation by $SOCl_2$, at a much slower rate, predominantly via a second-order mechanism (reaction 8) and not via a first-order mechanism (reaction 7) nor via loss of $SOCl_2$ (reaction 2) followed by reaction 1. In summary

$$k_1 = (2.1-5.0) \times 10^3\ M^{-1}\ s^{-1}$$

$$k_2 = (1.3-1.6) \times 10^4\ M^{-1}\ s^{-1}$$

$$k_{-2} \leq 1.7 \times 10^{-3}\ s^{-1}$$

$$k_3 \leq 1.6 \times 10^{-4}\ s^{-1}$$

$$k_4 = 1.51 \pm 0.50\ M^{-1}\ s^{-1}$$

$$K \geq 7 \times 10^6\ M^{-1}$$

at room temperature (23 ± 1 °C).

It was confirmed that the proposed mechanism fits the experimental data[55] and that only one molecule of $SOCl_2$ binds to $Co^{II}TnPc(2-)$.

Reactions 1 and 8 are two-electron reactions between $Co^{II}TnPc(2-)$ and $SOCl_2$. Kukushkin,[56] reviewing $SOCl_2$ reactions, reports quite a few two-electron reactions resulting in dichloro products. Whether these reactions represent true two-electron transfers or two stepwise, but concerted, one-electron transfers remains to be solved.

The presence of HCl drastically slows the oxidation reaction. As result of this, HCl-free conditions should dramatically improve the performance of a $Li/SOCl_2/(CoTnPc,C)$ battery.

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(54) The results of this study apply specifically to $Co^{II}Pc$, and it should be noted that $Co^{I}Pc$ is the active species in $Li/SOCl_2/CoPc$ batteries.[10] The authors predict, however, that the current would dramatically increase in an HCl-free $Li/SOCl_2/CoPc$ battery even more so than indicated by the kinetic studies involving $Co^{II}Pc$, because $Co^{I}Pc$ is less likely to bind $SOCl_2$ and is more basic than $Co^{II}Pc$.[13]

(55) A simpler mechanism, consisting only of reactions 1 and 2, does not fit the experimental data. When reaction 8 is added to the scheme, one obtains an expression for k_{obs} that is a function of the concentration of thionyl chloride. Reaction 8 also explains the observed stability of the $(SOCl_2)Co^{II}TnPc(2-)$ adduct when there is no free $SOCl_2$ in solution.

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