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Lawrence A. Tinker, and Allen J. Bard

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Electrochemistry in Liquid Sulfur Dioxide. 1. Oxidation of Thianthrene, Phenothiazine, and 9,10-Diphenylanthracene

Lawrence A. Tinker and Allen J. Bard*

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received October 31, 1978*

Abstract: Electrochemical investigations of liquid sulfur dioxide solutions at −40 °C are reported. Cyclic voltammetric and coulometric studies of the oxidations of thianthrene (TH), phenothiazine (PH), and 9,10-diphenylanthracene (DPA) in SO_2 containing 0.15 M tetra-*n*-butylammonium perchlorate show that all three compounds are oxidized in two reversible one-electron steps to their respective radical cations and dications. Controlled potential coulometric studies with reversal show that both the radical cations and dications of TH and PH are stable on the coulometric time scale (~2 h), but DPA dication is not.

Introduction

Liquid sulfur dioxide is a nonprotonic, acidic, dipolar solvent, of relatively low boiling point (−10 °C), and reasonably high dielectric constant (20.0 at −40 °C).[1] It possesses several properties that make it interesting for use as an electrochemical solvent for studying oxidations of organic species. It has an unusual ability to solvate covalent compounds, making the study of organic species easy. It is a poor nucleophile, and should permit the study of cations and dications without interference from solvent reactions.

Liquid SO_2 is relatively easy to handle and purify on a vacuum line and, since it is used at low temperatures, the rate of reactions of electrogenerated species is decreased. Electrolysis products are relatively easy to isolate, because the solvent is a gas at room temperature and can be removed easily. However, relatively few studies of electrochemistry in liquid SO_2 have been reported. The earliest reports were investigations of the bulk electrolysis of various inorganic salts.[2-6] Later studies on the stability of various electrode systems in SO_2 reported by Cruse[7] showed that the silver-silver chloride electrode was the most stable, although the potential drifted with time. The calomel electrode was reported to be unsuitable as a reference electrode; however, the hydrogen electrode was found to be stable and reproducible.

The first reports on the use of SO_2 as a solvent for voltammetry were those of Elving and co-workers,[8-11] who investigated different inorganic salts and organic compounds at the dropping mercury electrode and the cylindrical platinum electrode. They reported that no suitable background electrolytes were found for use in SO_2, and they attempted their studies in the absence of background electrolytes. This led to serious problems with high solution resistance and large amounts of uncompensated resistance. In general, the voltammetric waves they observed were not very reproducible and were ill defined in shape. More recently, however, Miller and Mayeda[12] used SO_2 in voltammetric studies of an electrooxidative rearrangement in which tetra-*n*-butylammonium perchlorate (TBAP) was employed as a background electrolyte. They reported that 0.2 M solutions of both TBAP and tetrapropylammonium hexafluorophosphate gave conductivities of 9×10^{-3} ohm^{-1} cm^{-1} and that 9,10-diphenylanthracene (DPA) could be oxidized in a reversible one-electron wave to a stable radical cation. In this paper we report on the voltammetric and coulometric oxidation of thianthrene (TH), phenothiazine (PH), and DPA in liquid SO_2 and demonstrate the formation of very stable radical cations and dications of these species in reversible voltammetric processes.

Experimental Section

In all experiments vacuum techniques were used to purify the SO_2 (to eliminate traces of oxygen and water) and to transfer it to the cell. The cell used for the voltammetric and coulometric studies was a standard three-compartment cell with a separate reference compartment similar in design to that reported for use in liquid ammonia.[17] The experimental results reported here were all obtained at a platinum disk working electrode (area, 0.074 cm^2) which was pretreated before each set of experiments by rinsing with nitric acid and then distilled water, and then polished with an alumina slurry (0.3 μm) on felt. The auxiliary electrode was constructed of platinum wire and platinum foil and was soaked in nitric acid, rinsed with distilled water, and dried prior to use. The working electrode in coulometric studies was a 4.0 cm × 4.0 cm platinum gauze, which was treated in the same manner as the auxiliary electrode. The reference electrode was in a separate compartment, which was saturated with silver nitrate and contained 0.15 M TBAP to decrease solution resistance. Silver nitrate is not very soluble in liquid SO_2 and has been shown to react slowly with SO_2 to form silver sulfate[1] (eq 1):

$$6AgNO_3 + 7SO_2 \rightarrow 3Ag_2SO_4 + 2(NO)_2S_2O_7 + 2NO \quad (1)$$

To determine if this reaction had any effect on the electrode potential, two reference electrodes were assembled in separate compartments of one cell. One compartment contained the usual TBAP-$AgNO_3$ mixture, and the other contained TBAP-Ag_2SO_4. SO_2 was then distilled into each compartment and allowed to equilibrate for approximately 1 h. The difference in the potential between the two electrodes was less than 10 mV. All potentials reported in this work are reported against this reference electrode system, which, because of difficulties in reproducing the exact volume of SO_2 in the reference compartment, was only reproducible to ±50 mV (denoted AgRE).

Anhydrous grade sulfur dioxide (Matheson Gas Products, Inc., Houston, Tex.) (99.99%) was further purified by washing with concentrated sulfuric acid to remove SO_3 and other noncondensable gases, and passed through two 45-cm columns packed with P_2O_5 on glass wool to remove trace amounts of water. The supporting electrolyte, TBAP (Southwestern Analytical Chemicals, Austin, Tex., polarographic grade), was vacuum dried at 100 °C and stored in a desiccator. Thianthrene (Aldrich Chemical Co., Milwaukee, Wis.) (97%) was sublimed and stored in a desiccator prior to use. Both DPA and PH had been used in previous experiments in this laboratory and were resublimed prior to use.

Procedure. Before each experiment a sufficient amount of supporting electrolyte was added to each compartment of the cell to make the concentration approximately 0.15 M. The reference electrode compartment was prepared as described above. The compound to be studied was weighed and placed in the sample container. The cell was then placed on the vacuum line and evacuated for approximately 20 h. SO_2 was released from the tank through all-glass lines to the washing bottle, passed through the drying columns, and condensed at −50 to −60 °C and allowed to equilibrate for approximately 1 h. The temperature of the 2-propanol bath was controlled by a Model LC-100 liquid cooler cryostat (FTS Systems, Inc., Stone Ridge, N.Y.) employing a Model TCH-1 temperature controller (±0.1 °C). Prior to the actual experimental work, the temperature of the bath was raised to −40 °C and all experiments were conducted at this temperature.

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Table I. Summary of Voltammetric Parameters for Oxidation of Thianthrene, Phenothiazine, and 9,10-Diphenylanthracene in Liquid Sulfur Dioxide[a]

	thianthrene		phenothiazine		DPA	
diagnostic parameter	first wave	second wave	first wave	second wave	first wave	second wave
E_{pa}, V vs. Ag|Ag^{+b}	+0.32	+0.90	−0.18	+0.50	+0.20	+0.73
$E_{pa} - E_{p/2}$, mV	44 ± 5	40 ± 5	43 ± 5	51 ± 5	50 ± 5	50 ± 5
$E_{pa} - E_{pc}$, mV	45 ± 5	44 ± 5	54 ± 5	60 ± 5	60 ± 5	60 ± 5
i_{pa}/i_{pc}	1.0	1.0	1.0	1.0	1.0	0.95
$i_p/v^{1/2}C$, μA s$^{1/2}$ V$^{-1/2}$ mM^{-1}	57		59		52	
diffusion coeff, cm^2 s^{-1}	7.4×10^{-6}		8.3×10^{-6}		6.6×10^{-6}	

[a] 0.15 M TBAP; $T = -40$ °C; platinum working electrode, $A = 0.074$ cm^2. [b] Reference electrode as described in the Experimental Section.

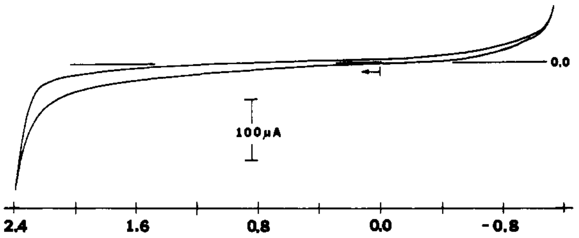

Figure 1. Cyclic voltammetric scan of the background at a platinum disk working electrode in 0.15 M TBAP-liquid sulfur dioxide at −40 °C, showing typical anodic and cathodic potential limits.

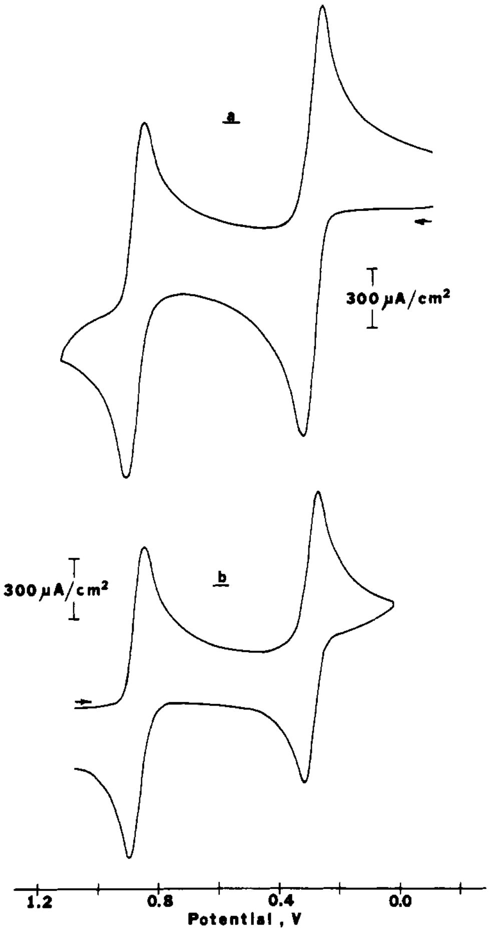

Figure 2. (a) Cyclic voltammetry of 2.51 mM TH in liquid SO$_2$-0.15 M TBAP at −40 °C. Scan rate was 200 mV/s. (b) After coulometric electrolysis of the same solution to give the dication solution. Scan rate was 200 mV/s.

All electrochemical measurements were made with a Model 173 potentiostat (Princeton Applied Research, Corp., Princeton, N.J.) employing positive feedback for iR compensation, a Model 175 universal programmer, and a Model 179 digital coulometer. Current-potential curves for scan rates (v) less than 500 mV/s were recorded on a Model 2000 X-Y recorder (Houston Instruments, Inc., Austin, Tex.). Those at scan greater than 500 mV/s were recorded with a Model 564 storage oscilloscope (Tektronix, Inc., Beaverton, Ore.).

Results and Discussion

Background. A typical cyclic voltammogram of the background current in liquid SO$_2$-0.15 M TBAP at −40 °C at a platinum disk electrode is shown in Figure 1. The useful potential range observed here is about −1.0 to +2.4 V vs. AgRE. The current observed at −1.0 V is probably due to reduction of SO$_2$ itself, while that at +2.4 V is probably that of oxidation of perchlorate ion. This wide range, extending to very positive potentials (to ca. +3.4 V on the conventional saturated calomel electrode scale, as shown below), makes this solvent particularly useful for studying electrochemical oxidations.

Thianthrene. A typical voltammogram observed for the oxidation of TH at a Pt disk electrode in SO$_2$ is shown in Figure 2a. The cyclic voltammetric characteristics, obtained for scan rates of 0.05 to 2.0 V/s, reported in Table I, are characteristic of one-electron Nernstian behavior for both waves; these thus correspond to the formation of the radical cation and dication of TH:

$$\mathrm{TH} \rightleftharpoons \mathrm{TH}^{+\cdot} + e^- \qquad (2)$$

$$\mathrm{TH}^{+\cdot} \rightleftharpoons \mathrm{TH}^{2+} + e^- \qquad (3)$$

The difference in the E^0 values for the two processes, calculated from the corresponding values of E_p, can be used to calculate an equilibrium constant, K_D, for the disproportionation reaction, eq 4:

$$2\mathrm{TH}^{+\cdot} \rightleftharpoons \mathrm{TH}^{2+} + \mathrm{TH} \qquad (4)$$

The 0.58-V difference yields $K_D = 4.4 \times 10^{-12}$ (−40 °C). Previous studies of TH species have shown that the value of K_D depends strongly upon the solvent system and the relative solvation of TH$^{+\cdot}$ and TH^{2+} and ranges from 7.6×10^{-8} in isobutyronitrile to 2×10^{-12} in a trifluoroacetic acid-trifluoroacetic anhydride medium.[21]

Controlled potential coulometry carried out at +0.50 V produced a dark purple solution and an n_{app} value (faradays per mole of reactant consumed) of 0.99. This corresponds to the one-electron oxidation of TH as described in eq 2. Voltammetric reduction of this solution showed that the radical cation was stable for at least several hours. The peak height of the reduction wave for TH$^{+\cdot}$ was always somewhat smaller than that for the original oxidation wave of the parent species. This was clearly not attributable to decomposition of TH$^{+\cdot}$, since the cathodic peak height did not change with time, and, when the radical cation solution was reduced coulometrically

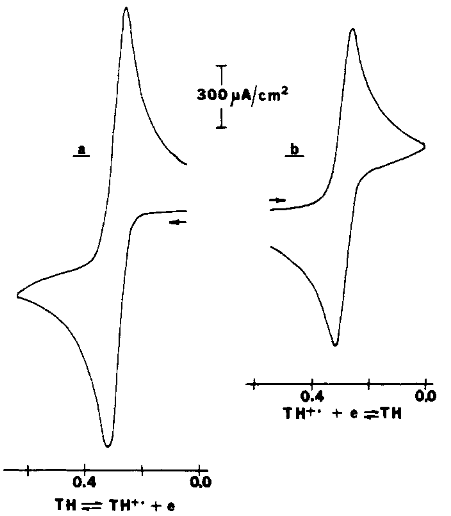

Figure 3. (a) Cyclic voltammetric scan of 3.21 mM TH in liquid SO_2–0.15 M TBAP at −40 °C encompassing only the first oxidation process. Scan rate was 200 mV/s. (b) After coulometric electrolysis to the radical cation illustrating change in peak current for reduction of $TH^{+\cdot}$. Scan rate was 200 mV/s.

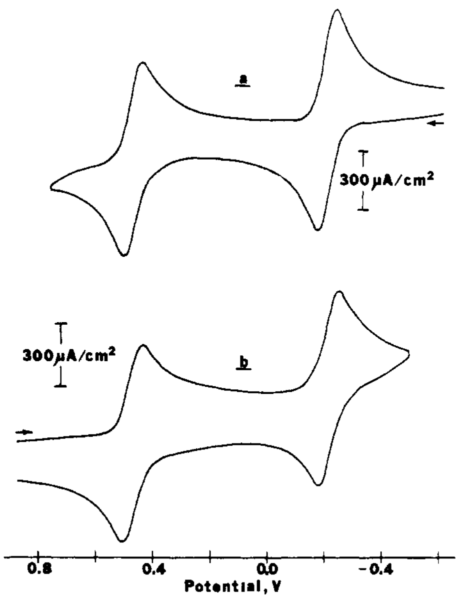

Figure 4. (a) Cyclic voltammetry of 1.53 mM PH in liquid SO_2–0.15 M TBAP at −40 °C. Scan rate was 200 mV/s. (b) After coulometric generation of the dication of PH. Scan rate was 200 mV/s.

back to the neutral TH, the anodic peak height again showed the original height. Since the analytical concentration of TH in solution had not changed and the temperature was the same for both waves, there is apparently a significant change in diffusion coefficient in going from the neutral compound to radical cation. To evaluate the diffusion coefficients of these two species more precisely, chronoamperometric experiments were carried out on the solution of the neutral compound and on the electrochemically generated radical cation. Values of $it^{1/2}$ were averaged for each run, and the diffusion coefficients were evaluated using the Cottrell equation.[18] The two values calculated were 7.4×10^{-6} cm²/s for the neutral compound and 3.3×10^{-6} cm²/s for the radical cation. This ratio of diffusion coefficients, when used in the equation for the peak current in cyclic voltammetry,[19] predicts that the i_{pc} for the radical cation will be ~70% that of i_{pa} of the neutral species, in reasonable agreement with the average experimental values found.

Two possibilities that exist which could explain this change in diffusion coefficient are dimerization of the radical cation (e.g., eq 5 or 6) or formation of a larger ion pair between $TH^{+\cdot}$ and perchlorate ion.

$$2TH^{+\cdot} \rightleftharpoons TH_2^{2+} \qquad (5)$$

$$2TH^{+\cdot} + 2ClO_4^- \rightleftharpoons (TH^{+\cdot}, ClO_4^-)_2 \qquad (6)$$

The formation of a dimeric species could easily explain the change in the diffusion coefficient, since formation of such a species would double the size of the diffusing electroactive species yielding peak heights in reasonable agreement with those found experimentally. Spectroscopic evidence for the formation of dimeric forms of $TH^{+\cdot}$. in various nonaqueous solvents has also been presented.[20] Moreover, such a difference in diffusion coefficients is not found with phenothiazine, as discussed in the next section, whose radical cation should show similar ion pairing properties.

Coulometric oxidation at +1.1 V to oxidize the neutral TH to the dication in one step yields $n_{app} = 1.98$ and produces a deep red-colored solution. Voltammetric analysis of the solution shows that the dication is also stable in SO_2 on a coulometric time scale (~2 h); this is the first reported stable solution of TH^{2+}. Two reversible reduction waves are observed (Figure 2b) with potentials essentially the same as those of the original solution. The peak heights of these two waves are close to those of the radical cation solution. Coulometric reduction of the dication solution yields 98% of the total number of coulombs generated on oxidation, and the peak height of the oxidation wave after coulometry returns to approximately the same height as that of the original solution.

Phenothiazine. A typical cyclic voltammogram observed for the oxidation of PH at a Pt disk electrode in liquid SO_2 is shown in Figure 4a. Two reversible one-electron waves are observed with the characteristics given in Table I, again indicating the successive formation of the radical cation and dication of PH:

$$PH \rightleftharpoons PH^{+\cdot} + e^- \qquad (7)$$

$$PH^{+\cdot} \rightleftharpoons PH^{2+} + e^- \qquad (8)$$

The E_p values yield a disproportionation constant for the radical cation, eq 9, $K_D = 2.4 \times 10^{-15}$.

$$2PH^{+\cdot} \rightleftharpoons PH^{2+} + PH \qquad (9)$$

The behavior of PH is very similar to that of TH, except that the cathodic peak height observed after controlled potential coulometric oxidation to $PH^{+\cdot}$ is almost the same as that for the original oxidation wave. The diffusion coefficient calculated for the neutral species from potential step chronoamperometric experiments is 8.3×10^{-6} cm²/s.

Controlled potential coulometry carried out in two steps gave n_{app} values of 0.98 for each wave. Voltammetric analysis after coulometric oxidation to PH^{2+} showed two reversible reduction waves at potentials corresponding to those for the original oxidations with the magnitudes of both waves being approximately the same as the original solution (Figure 4b).

Controlled potential coulometric reduction of the dication back to the parent compound occurred with the total number of coulombs obtained being 98% of that for the oxidation. The cyclic voltammograms of this regenerated solution were essentially the same as those of the original solution. Thus the results show a very stable radical cation and dication of PH in SO_2.

9,10-Diphenylanthracene. A typical cyclic voltammogram observed for the oxidation of DPA in SO_2–0.15 M TBAP at a Pt disk electrode is shown in Figure 5. Again two reversible one-electron waves were observed with the pertinent data listed in Table I, demonstrating the successive formation of the radical cation and dication:

$$\mathrm{DPA} \rightleftharpoons \mathrm{DPA}^{+\cdot} + e^- \qquad (10)$$

$$\mathrm{DPA}^{+\cdot} \rightleftharpoons \mathrm{DPA}^{2+} + e^- \qquad (11)$$

The difference in E_{pa} values of 0.530 V yields $K_D = 3 \times 10^{-12}$ at −40 °C, which is similar to that observed for TH and PH. In general, the behavior of DPA is similar to that of PH, and no significant change in peak height was observed when controlled potential coulometry was carried out at the first oxidation process. The diffusion coefficient calculated from potential step chronoamperometric data is $D_{DPA} = 6.3 \times 10^{-6}$ cm^2/s at −40 °C. This slightly smaller value for DPA as compared to TH and PH is consistent with the larger volume of DPA. Controlled potential coulometry carried out at +0.35 V, to oxidize completely the neutral species to the radical cation, gave an $n_{app} = 0.9$ and a blue colored solution. Voltammetric analysis after coulometry showed that DPA$^{+\cdot}$ is stable on a coulometric time scale. Controlled potential coulometry carried out at +1.0 V to oxidize DPA to the dication gave $n_{app} = 2.1$; however, the dication, DPA^{2+}, was not stable on a coulometric time scale and reacted to form a product that was harder to oxidize than DPA itself. This could be seen in the cyclic voltammetry following coulometry, where a new irreversible wave about 140 mV more positive than the original DPA$^{+\cdot}$/DPA^{2+} wave appeared; the original DPA oxidation waves were no longer visible.

Benzene. Oxidation of benzene in SO$_2$–TBAP at − 40 °C occurred in an irreversible wave with $E_{pa} = +1.65$ V vs. AgRE with filming of the electrode surface. None of the characteristic voltammetric data could be obtained because of the degradation of the electrode surface, which probably occurs by the polymerization of benzene forming a blocking film on the electrode. Attempts at coulometric oxidation of benzene solutions were also unsuccessful, with only a sharp current spike noted at the beginning of the electrolysis followed by rapid decay of the current to the background level within a few seconds.

If water was added to the solution in a 10–20 times excess of the amount of benzene, filming still occurred. The rate of the current decay to background during coulometry was much slower (∼10–15 min). This suggests that water participates in the reaction and that filming might be retarded with a larger excess of water present. Further studies of the oxidation of benzene–water mixtures are in progress.

Effect of Addition of Nucleophiles. Preliminary experiments have been run in which water was added as a nucleophile to the TH and DPA systems. The TH/TH$^{+\cdot}$ wave was not affected by the addition of an amount of water corresponding to ∼10 times the TH concentration, and coulometry carried out to oxidize TH to TH$^{+\cdot}$ completely gave $n_{app} = 0.98$. The radical cation was stable under these conditions. The TH$^{+\cdot}$/TH^{2+} wave, however, was perturbed, and a new oxidation wave appeared during cyclic voltammetric scans more positive than the TH$^{+\cdot}$/TH^{2+} wave, when water in amounts equimolar to the TH was added. This wave height increased with the addition of more water, and the peak current ratio for TH$^{+\cdot}$/TH^{2+} wave decreased. This suggests that the dicationic species reacts rapidly with water in SO$_2$. Addition of water in equimolar amounts to the DPA system caused no change in the cyclic voltammetry of the DPA/DPA$^{+\cdot}$ wave, but produced an increase in the height of the second wave and a decrease in the magnitude of i_{pc} on scan reversal for this wave. No new oxidation waves were observed, however. More detailed investigations of these reactions are in progress and will be reported in future articles in this series.

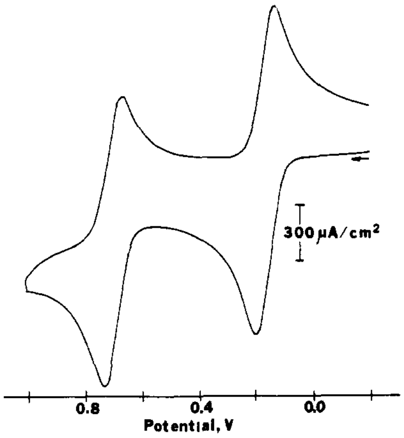

Figure 5. Cyclic voltammetric scan of 2.66 mM DPA in liquid SO$_2$–0.15 M TBAP at −40 °C. Scan rate was 200 mV/s.

Conclusions

The results reported here demonstrate that SO$_2$ is an excellent solvent for the study of electrochemical oxidations. The range of solvent stability extends to very positive values, making it especially useful for studies of species which are difficult to oxidize. An estimate of this positive range can be obtained by considering the potential of the DPA/DPA$^{+\cdot}$ wave in SO$_2$ (+0.2 V vs. AgRE) and in CH$_3$CN (+1.35 V vs. SCE). Since the assumption is usually made[22] that the solvent interactions with a large polynuclear aromatic hydrocarbon and its radical cation are nearly the same, one must ascribe a large part of the difference in potentials to differences in the reference electrode potentials. This then corresponds to an oxidation limit for SO$_2$ of about +3.4 V vs. SCE, which is well beyond that found for CH$_3$CN and other aprotic solvents often used in electrochemical investigations.[23,24] The low melting point of SO$_2$ (−72.7 °C) should also permit low-temperature electrochemical investigations leading to even better stability of electrogenerated intermediates.[25,26] The high stability of the dications of TH and PH suggests that this solvent is particularly attractive for the investigation of the physical and chemical properties of such species. Such studies are in progress.

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