Electrochemical and Spectroscopic Investigation of the Influence of Acid–Base Chemistry on the Redox Properties of 2,5-Dimercapto-1,3,4-thiadiazole

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The UV–vis spectroscopy and cyclic voltammetry of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) were studied in the absence and presence of pyridine (Py) or triethylamine (TEA) in acetonitrile solutions in order to examine the influence of acid–base processes on the redox behavior of DMcT. In solutions containing Py, DMcT can be singly deprotonated to give the anionic species, $DMcT^-$. In solutions containing TEA, DMcT can be either singly or doubly deprotonated to give the anionic species, $DMcT^-$, or the dianion, $DMcT^{2-}$, depending on the stoichiometry. These acid–base processes were monitored using UV–vis spectroscopy, and those results are reported here. The cyclic voltammetry of both systems was also examined in the absence and presence of Py or TEA. These experiments clearly showed that deprotonation of DMcT results in facilitation of its electrochemical oxidation, leading either to a disulfide-containing dimer or a disulfide-containing polymer, depending on conditions. The relevance of these results to the use of DMcT as a cathode material in lithium secondary batteries is discussed.

Introduction

We have been interested in the use of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) as part of an active cathode material for secondary lithium battery applications.[1–6] The results of several previous reports have suggested that acid–base chemistry plays an important role in the facilitation of the DMcT redox processes by polyaniline.[1,4] However, since the effects of proton transfer on the redox reactions of DMcT are still unknown, we have begun investigations into the fundamental acid–base chemistry of DMcT, as well as its influence on DMcT redox behavior. While DMcT is a remarkably versatile compound,[7,8] little basic information about its structure and general chemical reactivity exists in the literature.[9,10] Recent efforts by our groups to rectify this situation have included the assignment of the vibrational bands of DMcT in the solid state[11] and preliminary elucidation of the acid–base chemistry of DMcT in nonaqueous media.[4] In this contribution, we report investigations employing cyclic voltammetry and electronic spectroscopy to monitor acid–base equilibria between DMcT (and its conjugate bases) and two bases (i.e., pyridine and triethylamine) or an acid (methanesulfonic acid). Using these results, the influence of these acid–base processes on DMcT redox behavior has been elucidated. To our knowledge, this represents the first correlation of the acid–base chemistry of DMcT with its cyclic voltammetric and spectroscopic behavior.

Despite the paucity of fundamental studies on the acid–base properties of DMcT, there are several reports on its behavior in a variety of other areas. For example, DMcT has been widely studied as a metal chelating agent,[10,12–15] where UV–vis and vibrational spectroscopy were extensively used as diagnostic tools. Also, it is well-known that the thioamide groups in DMcT and several of its derivatives can exist in different tautomeric forms,[16–18] both in the solid state and in solution. It has also been reported previously that DMcT has aqueous dissociation constants of $pK_{a1} = -1.36$ and $pK_{a2} = 7.5$,[4] making its neutral

form a very strong acid and its anionic form a weak acid. The proton dissociation equilibria of DMcT are shown in Scheme 1, including the most likely tautomers (shown in parentheses). For example, in the dithiol (Scheme 1a) and monothiolate (Scheme 1b) forms, at least two tautomers are possible. While it is known from the crystal structure that DMcT exists mainly in the thione/thiol form in the solid state,[9] its structure in solution has yet to be thoroughly studied. We will report on this issue in a future contribution. For the purposes of the present report, the issue of tautomerization will be addressed for each individual case and set of conditions.

Experimental Section

Materials. Acetonitrile (AN) was purchased from Kanto Chemical Co., purified by distillation in the usual manner, and stored over 3Å molecular sieves. DMcT and 2-mercapto-5-methyl-1,3,4-thiadiazole (McMT) were purchased from Tokyo Kasei and used without further purification. Lithium perchlorate was used as purchased. Pyridine (Py), triethylamine (TEA), and methanesulfonic acid (MSA) were used as purchased from Kanto Chemical Co. The dipotassium salt of the dianion of DMcT ($DMcT^{2-}$) was used as purchased from Aldrich Chemical Inc.

Synthesis of Monolithium Salt of 2,5-Dimercapto-1,3,4-thiadiazole ($DMcT^-$). Lithium hydroxide monohydrate (0.56 g, 13.3 mmol) was dissolved in a methanol and water solution. The solution was purged of oxygen by bubbling with N_2 gas for 20 min. 2,5-Dimercapto-1,3,4-thiadiazole (2.0 g, 13.3 mmol) was added to the solution (under N_2). The solvents were removed by rotary evaporation, during which the yellow solution gradually became light orange, finally leaving an orange-yellow solid. The solid was recrystallized from methanol and dried under vacuum for 20 h at room temperature.

Synthesis of Bis(2-mercapto-1,3,4-thiadiazoyl)-5,5′-disulfane (di-DMcT). The structure of this compound is shown on the far right of Scheme 1b. A 200 mL round-bottom flask was charged with methanol (50 mL) and 2,5-dimercapto-1,3,4-thiadiazole (2.0 g, 13.3 mmol). To the reaction mixture was added a solution of iodine (1.69 g, 6.65 mmol) in methanol (20
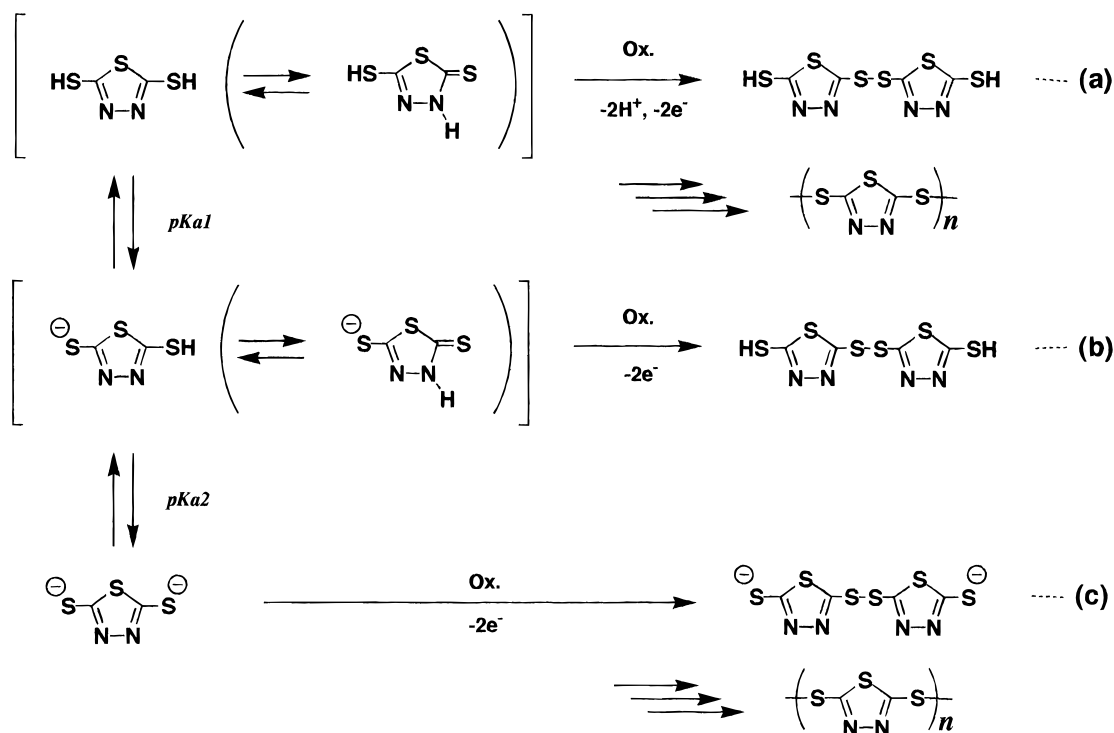
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SCHEME 1

mL) over 15 min with vigorous stirring (under N_2). After 1 h, the reaction mixture was poured into water. The precipitate was washed with water and recrystallized from methanol to leave a pale orange solid (1.75 g, 88% yield). Anal. Calcd for $C_4H_2S_6N_4$: C, 16.10; H, 0.68; N, 18.77; S, 64.45. Found: C, 16.08; H, 0.67; N, 18.75; S, 64.5.

Electrochemical Measurements. Cyclic voltammograms were obtained at room temperature using a Toho Technical Research potentiostat (Model PS-06) or a BAS CV-27 and are reported vs Ag/AgCl. Measurements were taken in a three-electrode cell configuration using a glassy carbon disk electrode (BAS, 3.0 mm diameter), a Pt coil counter electrode, and a Ag/AgCl reference electrode, against which all potentials are reported. Unless otherwise noted, all experiments were conducted in a 0.1 M $LiClO_4$ acetonitrile solution, which was extensively deaerated using nitrogen gas.

Electronic Spectroscopy Methods. UV−vis spectra were recorded using either a JASCO Model U-Best-55 or a Hewlett-Packard HP8452 diode array spectrometer in AN solution. Considerable care was taken to ensure the exclusion of both oxygen and water from the samples during these experiments.

Computational Methods. The spectral results were compared qualitatively against the results of quantum chemical calculations. PM3[19,20] calculations were done using the MO-PAC software with a PC (IBM PS/V, DX486 66 MHz). Initially, geometries were fully optimized using BFGS (Broyden−Fletcher−Goldfarb−Shanno)[21−24] and/or EF (Eigenvector following)[25] methods in the PM3 calculation. ZINDO[26,27] calculations were performed using the CAChe software system (CAChe Scientific, Inc.) on an Apple Macintosh PowerPC. As in the MOPAC calculations, the target structures were first fully optimized, then the UV−vis spectra were calculated using the INDO/1 (intermediate neglect of differential overlap) Hamiltonian (RHF, C.I. = 9).[28,29]

Results and Discussion

UV−Vis Spectra of DMcT. To unequivocally establish the acid−base chemistry of DMcT, the spectra of this compound were examined in AN solution in the absence and presence of
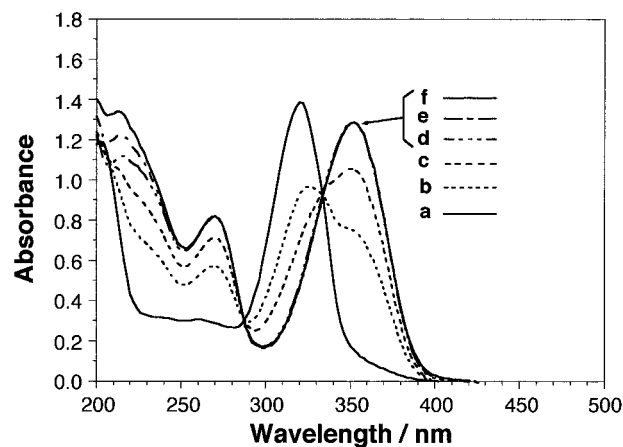

Figure 1. UV−vis spectra of a DMcT−TEA system in AN solution. [DMcT] = 1 mM. At the concentration ratio [TEA]/[DMcT]; (a) 0.0; (b) 0.5; (c) 0.75; (d) 1.0; (e) 1.5; (f) 2.0.

varying quantities of Py or TEA. Figure 1 shows the results of one such experiment in which a DMcT solution was titrated with TEA. Curve a shows the spectrum of 1 mM DMcT in AN. This spectrum has a prominent peak at 320 nm that is characteristic of the neutral (acid) form of DMcT.[18,30] Curves a−f show the results of addition of TEA to this solution, with curve d showing the spectrum after addition of 1 molar equiv of TEA. This spectrum shows peaks at 270 and 352 nm. Note the presence of two isosbestic points at 287 and 331 nm in this series of spectra, indicating a simple conversion from one form to another during the titration. Addition of an additional equivalent of TEA (curves d−f) ultimately produces the spectrum in curve f, which is remarkably similar to that resulting from addition of the first equivalent of TEA. Given that TEA has a pK_a of 10.7,[31] it should be a sufficiently strong base to produce both $DMcT^-$ and $DMcT^{2-}$ from DMcT. Thus, the similarity of curves d−f in Figure 1 suggests that $DMcT^-$ and $DMcT^{2-}$ have nearly identical spectra.

These spectra can be compared to the previously reported spectra of DMcT and several derivatives. For DMcT, Thorn[30] describes two prominent peaks at 260 and 335 nm (in ethanol)
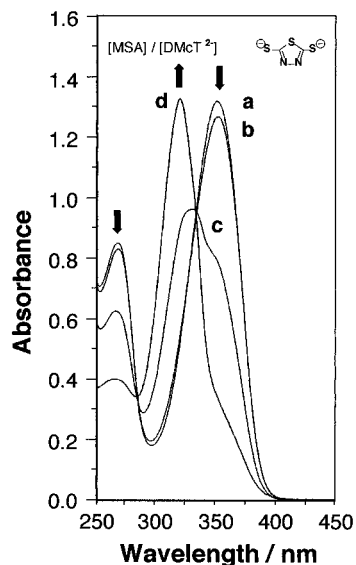
Figure 2. UV−vis spectra of DMcT^{2-}−MSA (methanesulfonic acid) system in AN solution. [DMcT^{2-}] = 1 mM. At the concentration ratio [MSA]/[DMcT^{2-}]: (a) 0.0; (b) 1.0; (c) 1.33; (d) 2.0.

with molar absorptivities of 5.1×10^3 and 1.4×10^4 M^{-1} cm^{-1}, respectively. However, this spectrum most closely resembles those shown in curves d−f in Figure 1, which we assign to the DMcT$^-$ and DMcT^{2-} species. This discrepancy is easily understood on the basis of the relative pK_a values of DMcT, acetonitrile, and ethanol, which are −1.36,[4] ca. −10, and ca. −2.[32] Thus, in dilute ethanol solutions, DMcT will behave as a strong acid and exist in a dissociated state (*i.e.*, as CH$_3$CH$_2$-OH$_2^+$ and DMcT$^-$). As a consequence, the spectrum reported by Thorn is almost certainly that of the DMcT$^-$ species. On the other hand, DMcT should exist as the undissociated (neutral) form in AN, which is not a sufficiently strong base to serve as an acceptor for the first deprotonation of DMcT. Thus, we assign the spectrum shown in curve a, Figure 1, to the neutral (undissociated) species, DMcT, that shown in curve d to DMcT$^-$ and that shown in curve f to DMcT^{2-}. We return to a discussion of the remarkable similarity of the DMcT$^-$ and DMcT^{2-} spectra below.

We also conducted an experiment that was done identically to that in Figure 1, except that Py was used as the added base (not shown). Again, one observes the appearance of peaks at 270 and 350 nm after the addition 1 mol equiv of base, and an essentially identical spectrum after the addition of the second equivalent. However, in this case, since the pK_a of Py is only 5.25,[31] it does not seem likely that Py would be capable of deprotonating DMcT$^-$ to produce DMcT^{2-}. While this issue is not clearly resolved by the spectra presented here due to the nearly identical spectra of DMcT$^-$ and DMcT^{2-}, as will be seen below, the electrochemical results do allow for its resolution.

As already suggested, these results can be interpreted to imply that the first molar equivalent of base produces DMcT$^-$, which exhibits peaks at 270 and 350 nm. Interestingly, they also suggest that DMcT^{2-}, which should be produced by addition of the second equivalent of TEA, has a spectrum that is nearly identical with that of the monoanion. This finding was sufficiently surprising that additional experiments were done to confirm it. One such experiment involved the titration of DMcT^{2-} to the monoanion and then to the neutral form with a strong acid, methanesulfonic acid (MSA), which has a pK_a of −1.86.[33] Figure 2 shows the spectrum of an authentic sample of DMcT^{2-} (curve a), as well as the spectra that result from addition of various amounts of MSA to the sample. Note that the spectrum in curve a is identical with those in curve f in Figure 1. Addition of 1 mol equiv of MSA produces the
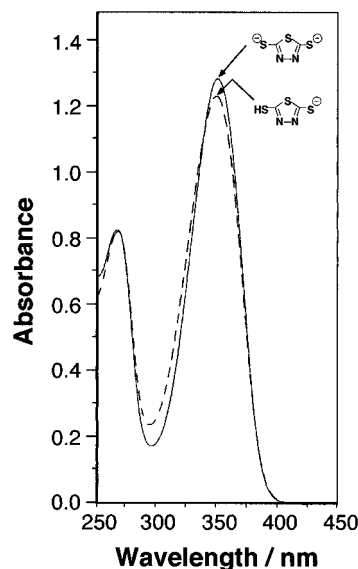

Figure 3. UV−vis spectra of DMcT$^-$ and DMcT^{2-} in AN solution, both at concentrations of 1 mM.

TABLE 1: Observed and Calculated λ_{max} (nm) of DMcT Derivatives

compounds	obs^a	calc^d
	320	319
	350	350
	352	362

^{a} In 1 mM acetonitrile. ^{b} Calculated by INDO/1.

spectrum shown as curve b in Figure 2. Given that MSA is a strong acid that should be capable of protonating DMcT^{2-}, it seems clear that curve b must represent the spectrum of DMcT$^-$, an interpretation that is consistent with the spectra presented in Figure 1. Addition of an additional equivalent of MSA produces the spectrum of neutral DMcT, as shown in curve d in Figure 2. Finally, Figure 3 shows a comparison of the spectra of an authentic sample of DMcT^{2-} and of a sample of DMcT$^-$ that was produced by mixing equimolar quantities of DMcT and DMcT^{2-}. Again, these curves are nearly identical, demonstrating the almost identical nature of the DMcT$^-$ and DMcT^{2-} spectra.

Further confirmation that DMcT^{2-} and DMcT$^-$ have substantially identical spectra was sought from the quantum chemical calculations using ZINDO. This semiempirical method is based on a series of electronic structure programs that have been developed over the past 20 years.[26] It employs a variety of electronic structure methods. For calculation of spectral data, the most commonly used model is of the INDO type. This model is well parameterized to agree with experimental spectra.[34−36] As can be seen in Table 1, INDO calculations suggest that the spectra of DMcT$^-$ and DMcT^{2-} should be very similar, and both should be significantly different from that of DMcT. It can also been seen in the Table 1 that the calculated and observed λ_{max} values are in good agreement. However, we note that since the experimental λ_{max} values are obtained in liquid phase and the calculated values are for the gas phase, this agreement could be coincidental. Nevertheless, if one compares the *relative* spectral shifts induced by the first and
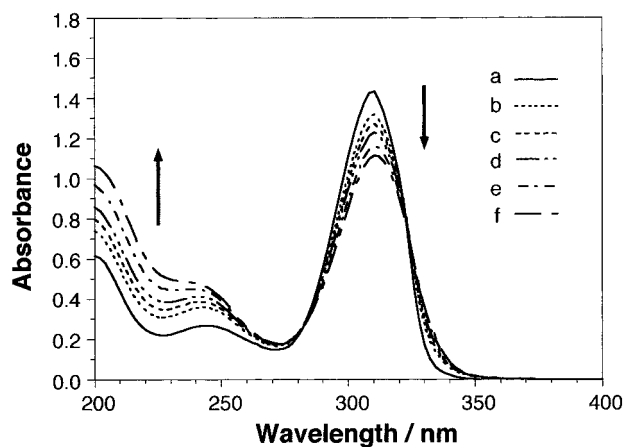
Figure 4. UV−vis spectra of a McMT−TEA system in AN solution. [McMT] = 1 mM. At the concentration ratio [TEA]/[McMT]: (a) 0.0; (b) 0.5; (c) 0.75; (d) 1.0; (e) 1.5; (f) 2.0.

second deprotonations, these calculations provide good support that the spectra of $DMcT^-$ and $DMcT^{2-}$ should be very similar.

UV−Vis Spectra of McMT. For comparative purposes, the acid−base chemistry of McMT was also investigated using UV−vis methods. Figure 4 shows the results of one such experiment. Curve a shows the spectrum of 1 mM McMT in AN solution. It exhibits a prominent peak at 305 nm, which is reasonably similar to that for DMcT (at 320 nm). Curves b−d show the spectra that result when TEA is added in an amount up to 1 mol equiv. Given that McMT has a pK_a of 5.35,[4] it is expected that TEA will produce the deprotonated form of McMT, $McMT^-$. As can be seen, there are only minor spectral changes during the addition of TEA. Thus, as was the case for $DMcT^-$ and $DMcT^{2-}$, the spectra of McMT and $McMT^-$ appear to be very similar.

Cyclic Voltammetry of DMcT. Given the acid−base chemistry between TEA and DMcT that was discussed above, we first examined the influence of TEA on the electrochemical behavior of DMcT. Curve a in Figure 5 shows the cyclic voltammetry of DMcT in AN solution containing 0.1 M $LiClO_4$ as supporting electrolyte. The data show a small oxidation peak at ca. 0.2 V and the corresponding reduction at ca. −0.2 V. On the basis of the large separation of the anodic and cathodic peaks, the process is judged to be electrochemically quasireversible. Further, given that the DMcT concentration in this experiment is 10 mM, the magnitude of these peaks is far too small for them to derive from the DMcT species itself. Given this, there are at least two reasonable possibilities for the origins of these peaks. First, they may derive from DMcT itself but be decreased in magnitude due to interfacial processes (such as film formation) that depress the currents below their expected values. Second, they may derive from $DMcT^-$ that is produced by proton transfer from DMcT to trace amounts of water in the supporting electrolyte. On the basis of the results presented below, the second possibility seems more likely.

Curves b−d in Figure 5 show the results of addition of 0.5, 1.1, and 2.0 mol equival of TEA to the solution. Curve b shows a simple increase in the magnitude of the same peaks that are
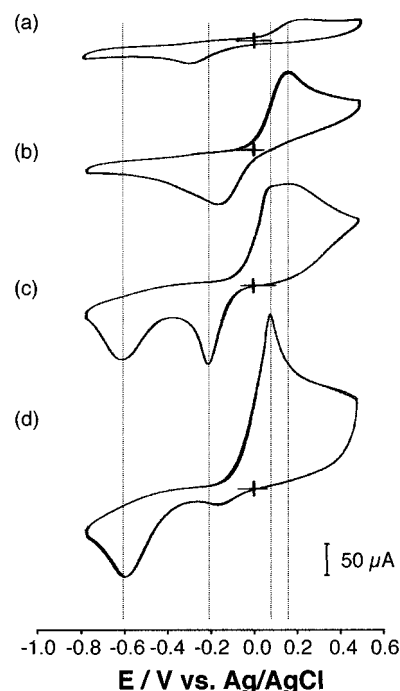

Figure 5. Cyclic voltammograms of a DMcT−TEA (a−b) system in AN solution. In the concentration ratio [TEA]/[DMcT] ([DMcT] = 10 mM): (a) 0.0; (b) 0.5; (c) 1.1; (d) 2.0. Scan rate = 50 mV/s, electrolyte 0.1 M $LiClO_4$. Vertical lines have been added to facilitate comparisons of peak positions in each voltammogram.
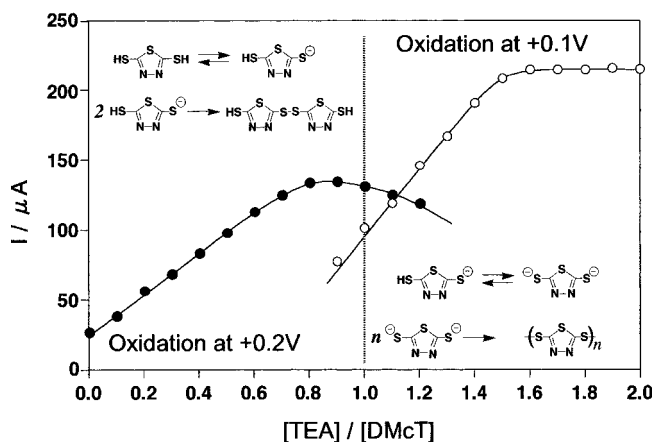

Figure 6. Plots of peak currents vs [TEA]/[DMcT] for oxidations at +0.2 V (●) and at +0.1 V (○).

observed in curve a. In this CV, the magnitude of the peaks is consistent with one-electron oxidation of 50% of the DMcT in the solution. Thus, it seems likely that these peaks derive from the one-electron oxidation of $DMcT^-$ and its subsequent reduction, in support of the second possibility discussed above for the origin of the peaks in curve a. The anodic peak at 0.2 V is therefore assigned to oxidation of $DMcT^-$ to produce the disulfide dimer (see Scheme 1b and Figure 6), and the cathodic peak at −0.2 V is assigned to the reverse of this process (Scheme 2a, i.e., reductive cleavage of the S−S bond in the dimer to
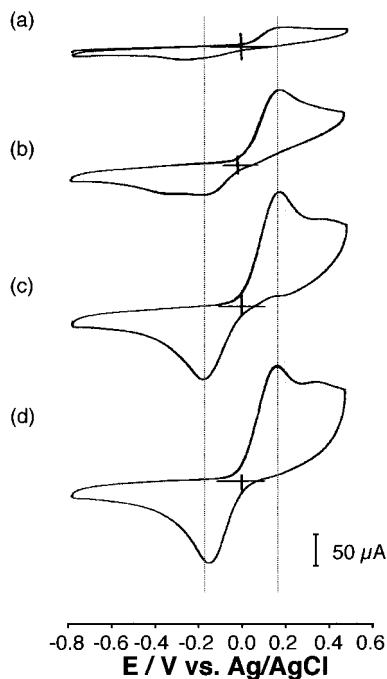
SCHEME 2

Properties of 2,5-Dimercapto-1,3,4-thiadiazole

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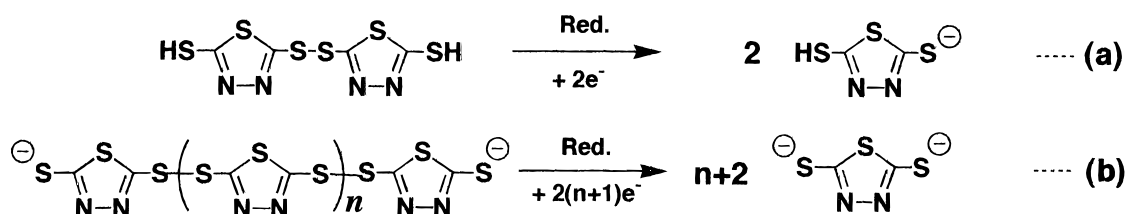
Figure 7. Cyclic voltammograms of DMcT−Py (a−d) system in AN solution. In the concentration ratio [Py]/[DMcT] ([DMcT] = 10 mM): (a) 0.0; (b) 0.5; (c) -1.0; (d) 1.5. Scan rate = 50 mV/s, electrolyte 0.1 M LiClO₄.

Figure 8. Cyclic voltammograms of DMcT dimer (5 mM) (a), DMcT (10 mM) in the presence of TEA (11 mM) (b), and DMcT^{2-} (dipotassium salt, 5mM) (c) in AN solution. Scan rate = 50 mV/s, electrolyte 0.1 M LiClO₄.

produce DMcT$^-$). When the TEA/DMcT molar ratio is increased to 1.1, a new peak appears at 0.1 V. The currents of these two sets of peaks are not as large as expected, probably due to film formation on the electrode surface that suppresses the electrochemical response of the system (see below). The magnitude of the new peak at 0.1 V increases up to a TEA/DMcT ratio of 2.0, after which it remains constant. Coincident with the appearance of this peak, a new cathodic peak appears at −0.6 V whose magnitude parallels that of the anodic peak at 0.1 V. Figure 6 shows a plot of the (uncorrected) peak currents for the 0.1 and 0.2 V anodic peaks versus the TEA/DMcT molar ratio, along with the suspected processes responsible for each. Specifically, we assign the 0.2 V peak to the oxidation of DMcT$^-$ to the disulfide dimer (Scheme 1b) and the 0.1 V peak to the oxidation of DMcT^{2-} to the disulfide polymer (Scheme 1c). These assignments are consistent with the acid−base chemistry with TEA, as discussed above. Further, the unusual sharpness of the 0.1 V peak is suggestive of "phaselike" behavior,[37−39] which might be expected due to the precipitation of the disulfide polymer on the electrode surface. In this paradigm, the cathodic peak at −0.6 V is most likely to derive from the reduction of the disulfide polymer back to the dithiolate species (Scheme 2b, i.e., where reductive cleavage of the disulfide bond occurs without protonation of the resulting thiolate).

Figure 7 shows the results of a similar experiment using Py as the base. Again, curve a shows the CV in the absence of Py. Curves b−d show the results for Py/DMcT molar ratios of 0.5, 1.0, and 1.5, respectively. As expected from the spectroscopic results above, the changes in the voltammetry are essentially identical with the TEA case up to a molar ratio of 1.0. However, increasing the Py concentration beyond this point does not lead to significant changes in the voltammetry. This suggests that Py cannot remove the second proton from DMcT (i.e., cannot deprotonate DMcT$^-$), a finding that resolves the issue raised in the discussion of the spectroscopic results above.

To confirm these assignments, the voltammetry of authentic samples of the disulfide dimer and of DMcT^{2-} was also examined (in the absence of any added acids or bases) and is
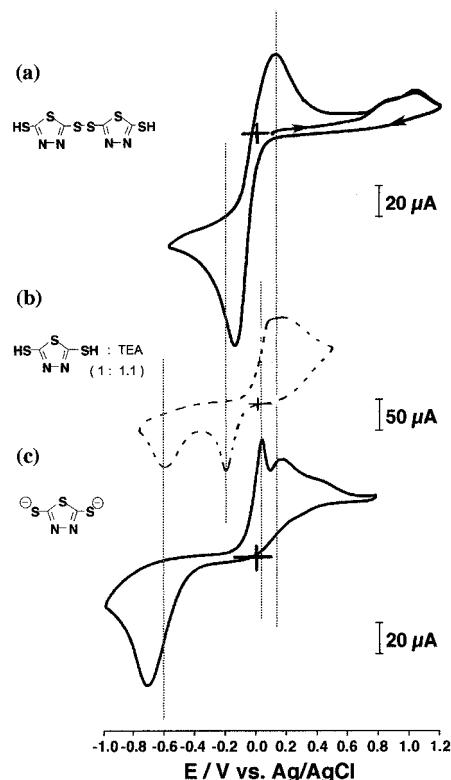
shown in Figure 8. Curve a is the CV of a solution of the disulfide dimer. Curve b is a reproduction of the data in curve c, Figure 5. Curve c is the CV of a solution of DMcT^{2-}. Curve a clearly shows the cathodic peak at −0.2 V and anodic peak at 0.2 V, both of which were attributed above to the reduction (Scheme 2a) and subsequent oxidation (Scheme 1b), respectively, of the disulfide dimer. Curve c shows that the sharp anodic peak at 0.1 V and the cathodic peak at ca. −0.6 V are characteristic of the oxidation (Scheme 1c) and subsequent reduction of DMcT^{2-} (Scheme 2b), respectively. The coincidence of these processes with those observed for the TEA/DMcT system is demonstrated by comparison with curve b. Thus, these results are in complete accord with the discussion presented above.

To further elucidate the influence of acid−base chemistry on the electrochemical behavior of DMcT, the influence of addition of Py on the voltammetry of DMcT was reexamined, this time over a more extended potential range. The results are shown in Figure 9. Curve a shows the CV of DMcT in the absence of Py. It is similar to those discussed above, except that a large anodic peak is observed at ca. 1.0 V due to the increased potential window for this scan. This peak is attributed to the direct oxidation of DMcT, presumably to the disulfide dimer (Scheme 1a). Thus, the increased driving force required for the oxidation of neutral DMcT compared to DMcT$^-$ of ca. 0.8 V is judged to be a direct result of the presence of the proton on the thiol group in DMcT. Addition of 0.5 mol equiv of Py results in curve b, which shows an increase in the anodic peak at ca. 0.2−0.3 V and a corresponding reduction in the peak at 1.0 V. Increasing the amount of Py to give a 1:1 molar ratio results in curve c, which is essentially the same as curve c in Figure 7. Both are also essentially identical with the CV of an authentic sample of DMcT$^-$, which is shown in curve e. Further increases in Py to a Py/DMcT molar ratio of 2.0 give curve d, which shows the appearance of a new anodic peak at 0.65 V that is present only at Py/DMcT molar ratios above 1.0. This
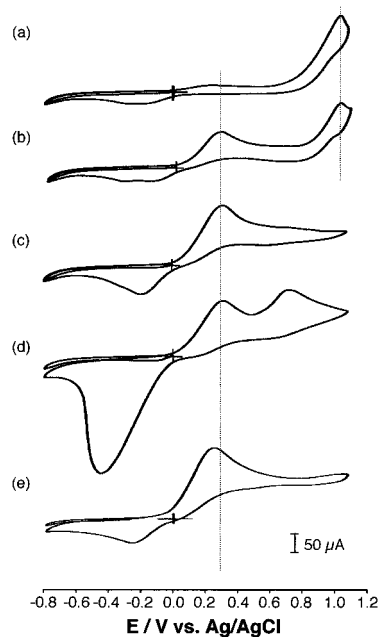
Figure 9. Cyclic voltammograms of DMcT−Py ([DMcT] = 10 mM) (a−d) system, DMcT⁻ (lithium salt, 10 mM) (e). In the concentration ratio of [Py]/[DMcT]: (a) 0.0; (b) 0.5; (c) 1.0; (d) 2.0. Scan rate = 50 mV/s, electrolyte 0.1 M LiClO$_4$.

peak is attributed to the Py-assisted oxidation of the disulfide dimer produced in the first anodic process, presumably to the disulfide polymer. Coincident with the appearance of this peak is the observation of a large cathodic peak at ca. −0.4 to −0.6 V which has the expected characteristics of a surface wave. This is attributed to the reduction of the disulfide polymer that, due to its very low solubility in AN, is present as a precipitate on the electrode surface. Electrochemical quartz crystal microbalance studies are currently in progress to verify the production and dissolution of the expected polymeric surface film during these processes.

The nature of the influence of Py on the oxidation of the disulfide dimer discussed above is not yet clear, but there are at least three possibilities. First, Py could be deprotonating the dimer to produce its conjugate base, which is then oxidized at a potential of 0.65 V to produce the disulfide polymer. Second, Py could be entering into a hydrogen-bonding interaction with the disulfide dimer that facilitates its oxidation. Third, Py could simply be acting as a base that accepts the proton(s) that is (are) lost from the disulfide dimer coincidentally with its oxidation. In this latter case, the Py is simply acting as a buffer in the nonaqueous solvent system, thus preventing increases in the proton activity near the electrode surface that would otherwise act to inhibit the oxidation process. These three possibilities are currently being investigated.

Conclusions

This study has elucidated the acid-base chemistry of DMcT via both UV−vis spectroscopic and cyclic voltammetric measurements. Specifically, the results reported here reveal how changes in the state of protonation of DMcT can lead to significant changes in the potentials at which its oxidation occurs, as well as in the products of the oxidation. For example, oxidation of DMcT at 1.0 V or of DMcT⁻ at 0.2 V occurs via extraction of one electron per molecule and produces the disulfide dimer shown in Figure 6. This difference in the driving force for the oxidation is clearly due to the state of protonation of the thiol group, a finding that is consistent with at least one previous study of thiol (thiolate) oxidations.[40] On the other hand, oxidation of DMcT²⁻ at 0.1 V produces the disulfide

polymer that has been argued to be present in the charged state of the lithium secondary cathode material in the battery studies[1−6] that provided the motivation for this work. An important conclusion of this study is that the state of protonation of DMcT, as well as its interactions with and/or proximity to bases, can have a very significant impact on the potentials at which its oxidation(s) occur. Thus, the function of polyaniline in the DMcT/polyaniline secondary cathode composite material may involve more than simple redox interactions; it may also involve acid−base chemistry. This issue is the subject of additional, ongoing investigations that will be reported in future contributions.

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