molecular electron transfer may occur from sulfur to the hydroperoxide moiety, most feasibly via a Fenton-type mechanism[16] in Ia (eq 4). Sulfoxide formation in this case constitutes an overall

$$I/Ia \rightarrow R(Hal)O^\bullet + Me_2SO\ (+H_2O) \qquad (4)$$

two-electron transfer and does not involve the 1e intermediate. Evidence for $R(Hal)O^\bullet$ is indicated through $Cl^\bullet$ atoms (from β-cleavage) which can be trapped by 1,1-dichloroethene and which, via reaction with *tert*-butyl alcohol,[17] increase the contribution of $^\bullet OOCH_2CMe_2OH$-induced DMSO formation.[18] Direct transfer of an oxygen atom is disregarded since $R(Hal)^{18}O^{18}O^\bullet$ did not yield any ^{18}O-labeled DMSO.

On the basis of our proposed mechanism, the 2e-process yield amounts to $G = 0.35$ (13% of $CCl_3OO^\bullet$) in the $CCl_4/10^{-3}$ M Me_2S system, $G = 1.8$ (65% of the $CHCl_2OO^\bullet$) in the $CHCl_3/10^{-3}$ M Me_2S system, and $G = 1.4$ (50% of $CHCl_2OO^\bullet$) in the $CHCl_3/7.4 \times 10^{-3}$ M Me_2S system.[19]

Degradation of $R(Hal)OO^\bullet$ results in quantitative dehalogenation irrespective of the donor, yielding $H^+/Cl^-/CO_2$ and $H^+/Cl^-/HCOO^-$ from CCl_4[8] and $CHCl_3$[20] systems, respectively. The route leading to the additional conductivity in the sulfide-containing solutions is considered to be the 2e process, which via the oxy radical liberates the same ions as the hydroperoxide but at a much faster rate. In full support of our mechanism, the yields of conductivity from complete $R(Hal)O^\bullet$ degradation[21] match the DMSO yields from the 2e process.

Positivation of sulfur in I favors reaction 3 and increases with halogenation of the peroxyl moiety. Electron transfer in Ia (reaction 4) should follow the opposite trend. This explains why the 2e yield is higher from $CHCl_2OO^\bullet$ than from $CCl_3OO^\bullet$.[22] Lower yields of the 2e process at higher sulfide concentrations are in accord with the competition between reactions 3 and 4.

In conclusion, halogenated peroxyl radicals, besides being good one-electron oxidants, can also undergo two-electron processes with certain compounds like sulfides, avoiding the 1e intermediate as free species but requiring adduct formation. One general reason to postulate this adduct as the all-important intermediate is that free $Me_2S^{\bullet+}$ and $(Me_2S\therefore SMe_2)^+$ are only known as oxidants but not reductants[23] and accordingly would not be able to efficiently transfer a second electron to the hydroperoxide (in this case also free). Our present results and conclusions complement electrochemical findings which not only discuss electrode-bound $Me_2S(OH)$ intermediates (rather than free radical cations) in sulfide oxidation[24] but also indicate an overall fast 2e process since less positive potentials are required for oxidation of the 1e intermediate than for the sulfide itself,[25] and our results demonstrate the favorable influence (and need) of water for electrochemical sulfoxide formation. Our results also relate to sulfoxide formation by other oxidizing, especially reactive oxygen, species via mechanisms which, to some extent, are still under discussion.[26-35]

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(19) Two-electron yield = total DMSO − 1e process $(Me_2S\therefore SMe_2^+)$ − $^\bullet OOCH_2CMe_2OH$ ($^\bullet OH$ and $Cl^\bullet$) contribution.

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(22) DMSO via a 2e process is also indicated from Me_2S reaction with $CH_2ClOO^\bullet$ and $CH_3OO^\bullet$. Quantitative evaluation on the basis of conductivity results and $(S\therefore S)^+$ formation was not possible since formation rates were too slow for pulse radiolysis experiments.

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The Complementary Redox Properties of Viologens and Pyromellitimides: A New Class of Organic Conductors

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Organic charge-transfer (CT) salts[1] have been of interest for some years, especially since the discovery of the metallic conductivity of the TTF–TCNQ salt.[2] We have begun an investigation of the charge-transfer chemistry of viologens and pyromellitimides, based on their complementary redox properties, with the intention of proceeding from intermolecular examples to intramolecular CT salts[3] and finally to examples in which the viologens and pyromellitimides are incorporated in a polymer. We report progress in the first two stages of this investigation, including isolation of a new, highly conductive intermolecular CT salt and electrochemical characterization of a covalently linked viologen/pyromellitimide. These studies point to an interesting new class of organic solid-state materials.

The ability of the violene[4] family of compounds to exist in three distinct oxidation states is well-known. Recent pioneering work by Haushalter and Kraus[5] and Mazur,[6] which has been extended by Viehbeck et al.,[7] has established that pyromellitimides can also

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Table I. Reduction Potentials[a] for **1** and **2**

compd	${}^1E_{1/2}$, V	${}^2E_{1/2}$, V
1	−0.370	−0.752
2	−0.685	−1.392

[a] Reduction potentials measured by cyclic voltammetry vs SCE at 0.5 mM in DMF/0.1 M Bu_4NBF_4.

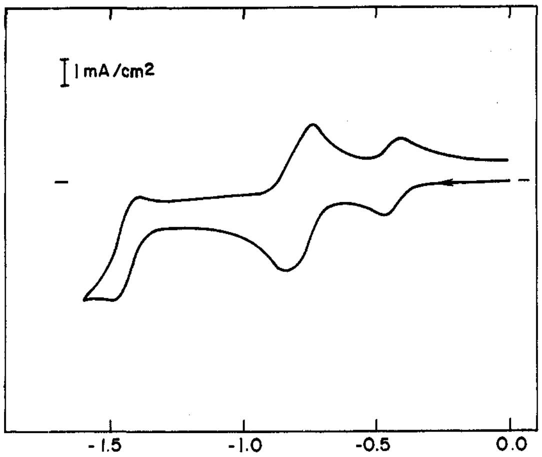
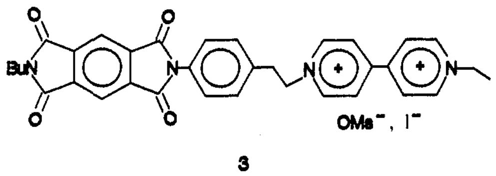


Figure 1. Cyclic voltammetry of 1 mM **3** in DMF with 0.1 M Bu_4NBF_4 at 50 mV/s. Voltages are vs SCE.

display three distinct oxidation states. The complementary charges and overlapping reduction potentials (see Table I) imply that a molecule in which both a viologen and a pyromellitimide are incorporated would, under reducing conditions, first add an electron to the viologen unit, generating a radical–cation, and then add a second electron to the pyromellitimide, leading to a radical–cation/radical–anion.

This possibility has been explored first by cyclic voltammetry (CV) and later by spectroelectrochemistry in dimethylformamide (DMF) containing 0.1 M Bu_4NBF_4. Both compound **3**,[8] in which the two moieites are covalently linked, and an equimolar mixture of diethyl viologen diiodide (**1**) and *N*,*N*′-dibutylpyromellitimide (**2**) were studied. The CVs for both **3** (Figure 1) and the **1**/**2** mixture can be readily understood as a superposition of the CV of the imide on that of the viologen. Note that the middle peak is roughly twice the height of the other two peaks because it is the result of two redox couples—the first imide reduction and the second viologen reduction—being poorly resolved in the CV.

Bulk electrolysis of **3** (N_2 glove box) at −0.6 V (vs saturated calomel electrode, SCE) generated the characteristic spectrum of the viologen radical–cation. The solution was then reduced further until a rest potential of $E_{soln} = -0.70$ V was attained, which resulted in a species showing absorptions for both the viologen radical–cation and the pyromellitimide radical–anion (Figure 2). Successive electrolyses to $E_{soln} = -0.75$, -0.79, and -1.40 V led first to the disappearance of the radical–cation absorption and appearance of absorptions of the neutral quinoid form of the viologen and then to disappearance of the pyromellitimide radical–anion absorption and appearance of the dianion absorption. Thus, the electrochemistry of **3** traverses five states: colorless dication, blue radical–cation, blue-green radical–cation/radical–anion, green radical–anion, and rose dianion.



3

The radical–cation/radical–anion state is an unusual[3] structure for an organic molecule in its ground state, i.e., a state not populated via photoexcitation. From both the CV and UV–vis results, it is clear that there is little interaction between the unpaired electrons, as might have been predicted from the length and relative rigidity of the aralkyl linkage.

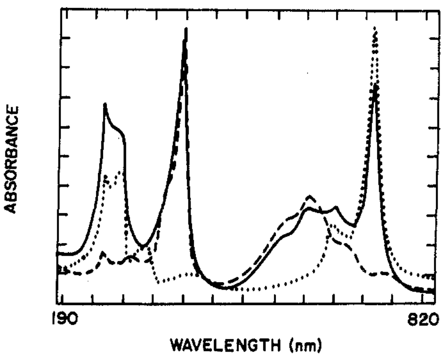


Figure 2. UV–vis spectra recorded by diode array detection: (---) 0.05 mM **1** in DMF with 0.1 M Bu_4NBF_4 after bulk electrolysis to $E_{soln} = -0.6$ V; (···) similar soln of **2** at $E_{soln} = -1.0$ V; (—) similar solution of **3** at $E_{soln} = -0.70$ V.

Bulk electrolysis on a solution of the viologen was also performed until it was completely converted to the neutral form ($\mathbf{1}^0$). At this point, addition of an equimolar amount of the unreduced imide (eq 1) resulted in a UV–vis spectrum very similar to that of doubly reduced **3**.

$$\mathbf{1}^0 + \mathbf{2} \rightleftharpoons \mathbf{1}^{\bullet-} \qquad (1)$$

With the above experiments in electrolyte solution serving as our entry into the CT chemistry of viologens and pyromellitimides, we turned next to the solid state. Using the reported[9] synthesis of $\mathbf{1}^0$ free of electrolyte, we prepared an equimolar solution of $\mathbf{1}^0$ and **2** in dimethoxyethane. Precipitation with *n*-heptane resulted in a purple, air-sensitive powder whose conductivity in pressed pellet form was 10^3–10^4 Ω^{-1} cm^{-1} (four-point probe under argon). Dissolution of this compound in DMF/0.1 M Bu_4NBF_4 resulted in the characteristic visible absorptions of both the viologen radical–cation and the pyromellitimide radical–anion, providing good evidence for assigning it the structure of a CT salt of $\mathbf{1}^0$ and **2**.[10]

Further characterization of this material, including its low-temperature electrical behavior, is underway. It is worth noting, however, that its room temperature conductivity even in pressed pellet form[11] is significantly higher than that of single crystals of many other organic conductors, including TTF–TCNQ,[1c] and is comparable to that of doped polyconjugated polymers such as poly(acetylene).[12] Extensions to the intramolecular CT salt form of **3** and to polymeric versions are of interest, and it is anticipated that significant elaboration of this new class of CT salts can be achieved by adjusting the redox potentials of both components by structural variation, for which ample possibilities exist.[1d,4,6,7,13]

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Supplementary Material Available: Synthetic procedures and spectral data for **3** and the CT salt (6 pages). Ordering information is given on any current masthead page.

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(8) See supplementary material.

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(10) Coulometry of the salt in the electrolyte solution was thoroughly consistent with a 1:1 ratio of the constituents. We have been unable to obtain a satisfactory elemental analysis of the salt, but an NMR spectrum obtained after dissolution of the salt in DMF-d_7 containing excess I_2 was readily identified as that of a 1:1 mixture of **1** and **2**.

(11) Pressed-pellet conductivities are commonly expected to be as much as a factor of 10^2 lower than that of single crystals of the same material; e.g.: Bringley, J. F.; Fabre, J.-M.; Averill, B. A. *J. Am. Chem. Soc.* **1990**, *112*, 4577–4579.

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