Photolysis of $R^1R^2NCH_2SPh$ with *t*-BuHgCl/KI in Me_2SO forms **2** (65%) and *t*-BuSPh (75%) while $PhNHCH_2SPh$ yields $PhNHCH_2CMe_3$ in 61% yield. In Scheme I an organomercurial serves as both an oxidizing agent (*t*-BuHgX in step 2) and a reducing agent (*t*-$BuHgI_2^-$ in step 4). (The value of $K_{complexation}$ for *t*-BuHgI and I^- is ~1 M^{-1} in Me_2SO.[3]) The reaction fails to occur in the absence of iodide ion required for the reduction step.

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Halogenated Peroxyl Radicals as Two-Electron-Transfer Agents. Oxidation of Organic Sulfides to Sulfoxides

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Halogenated peroxyl radicals, R(Hal)OO•, are known as efficient one-electron oxidants.[1] Rate constants for such 1e reactions generally increase with the degree of halogenation and depend on the redox potentials of the donors.[2-4] Exceptions to these trends have, however, been noted for some R(Hal)OO•-induced sulfide and selenide oxidations.[5,6] In this communication we provide evidence that R(Hal)OO• may also be involved in two-electron-transfer processes and that in the case of sulfide oxidation this is a direct route to sulfoxide.

Figure 1a shows the time-resolved conductivity change obtained upon pulse radiolysis of an aqueous, air-saturated, pH 4 solution containing 5×10^{-3} M CCl_4, 8×10^{-5} M chlorpromazine (CPZ), and 1.0 M *tert*-butyl alcohol. Dissociative electron capture by CCl_4 yields 1 equiv of H^+/Cl^- ions, evidenced by the fast increase in conductivity during the 1-μs pulse.[7] The $CCl_3OO^•$ radical formed by O_2 addition to $^•CCl_3$[8] oxidizes CPZ in a 1e process:[3]

$$CCl_3OO^• + CPZ + H^+ \rightarrow CPZ^{•+} + CCl_3OOH \qquad (1)$$

The $CPZ^{•+}$ is identified by its optical absorption (λ_{max} = 515 nm).[9] The associated decrease in conductivity reflects the replacement of the highly conducting protons by the less conducting $CPZ^{•+}$ radical cations[10] and shows that the hydroperoxide does not decay into ionic species over the experimental time scale. Qualitatively the same (with lower rates) applies for $CHCl_2OO^•$ radicals.

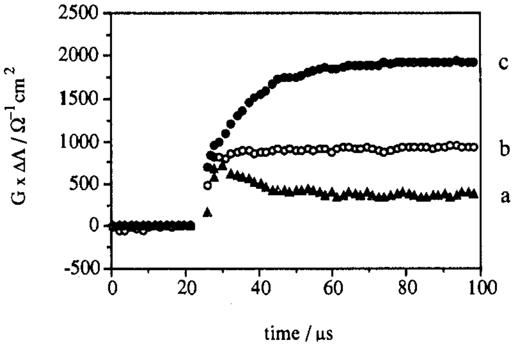
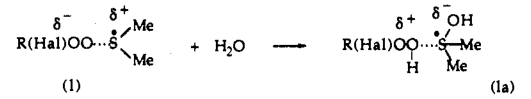


Figure 1. Conductivity (in units of $G \times \Delta\Lambda$) vs time trace obtained upon pulse radiolysis (pulse length ≈ 1 μs) of an aqueous, air-saturated, 1.0 M *tert*-butyl alcohol solution containing (a) 5×10^{-3} M CCl_4 and 8×10^{-5} M chlorpromazine (CPZ), pH 4.1; (b) 5×10^{-3} M CCl_4 and 1.0×10^{-3} M Me_2S, pH 4.0; and (c) 1×10^{-2} M $CHCl_3$ and 7.4×10^{-3} M Me_2S, pH 4.3.

One-electron oxidation of dimethyl sulfide by R(Hal)OO• leads to $(Me_2S\therefore SMe_2)^+$ radical cations (λ_{max} = 465 nm)[11] with yields of ≈75% and ≈50% for $CCl_3OO^•$-induced (10^{-3} M Me_2S, $k = 1.8 \times 10^8$ M^{-1} s^{-1})[5] and $CHCl_2OO^•$-induced (7.4×10^{-3} M Me_2S, 1.0×10^7 M^{-1} s^{-1}) reactions, respectively. The corresponding conductivity signals (Figure 1, parts b and c), in comparison to the CPZ system, show formation of additional yields of charged species. Thus, the net decrease caused by 1e oxidation is practically compensated in the CCl_4/Me_2S system, while in the $CHCl_3/Me_2S$ system the final conductivity (rising with the same rate as the 1e process) attains even more than twice the initial signal.

High yields of dimethyl sulfoxide are generated in our $CCl_4/CHCl_3$–O_2–Me_2S–Me_3COH systems,[12] e.g. (in terms of *G* units[13]): *G*(DMSO) = 2.1 in $CCl_4/10^{-3}$ M Me_2S, 3.55 in $CHCl_3/10^{-3}$ M Me_2S, and 5.0 in $CHCl_3/7.4 \times 10^{-3}$ M Me_2S systems. Part of it results from sulfide oxidation through $^•OOCH_2CMe_2OH$ radicals and by decay of the 1e intermediate $[Me_2S\therefore SMe_2]^+$. The respective contributions are calculable on the basis of experiments on exclusive Me_2S oxidation by •OH or $^•OOCH_2CMe_2OH$, respectively.[14] The remainder, which also results from R(Hal)OO• but not via the 1e mechanism, accounts for *G* = 0.45, 2.4, and 2.25 in the above three systems, respectively.

All observations concerning the sulfide oxidation are accounted for by assuming an adduct formation as the first step. The resulting sulfuranyl-type radical is likely to be polarized (I), possibly in "hydrated" form (Ia) (after inclusion of OH^- and H^+ and reversal of polarization): The addition formally constitutes a



$$R(Hal)OO^{\delta-}\cdots\dot{S}^{\delta+}Me_2 + H_2O \longrightarrow R(Hal)O^{\delta+}O(H)\cdots\dot{S}(O^{\delta-}H)Me_2 \qquad (2)$$

(1) (Ia)

1e oxidation of the sulfide function. A displacement reaction with a second sulfide (eq 3) receives its driving force from the stabilization of the three-electron bond.[11,15] Alternatively, an intra-

$$I/Ia + Me_2S \rightarrow (Me_2S\therefore SMe_2)^+ + R(Hal)OO^- (+H_2O) \qquad (3)$$

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(12) Analysis was performed on HPLC using an Inertsil column (250 × 4.6 mm, 5μ, ODS II) and UV detection at 210 nm. The eluent was isocratic methanol/water (5:95, v/v) at 1 mL/min. Radiation chemical conversions were generally kept to ≤10% to avoid secondary reactions to, e.g., higher oxidation states such as sulfones.

(13) *G* denotes the number of molecules generated/100 eV absorbed radiation energy. Initial R(Hal)OO• (from e_{aq}^- + halocarbon reaction) and $^•OOCH_2CMe_2OH$ (from •OH + *tert*-butyl alcohol) yields are *G* = 2.8.

(14) For •OH reactions irradiations were carried out with N_2O/O_2 (4:1 v/v) saturated solutions, 1×10^{-3} M Me_2S, pH 6; for $^•OOCH_2CMe_2OH$ reactions solutions were air-saturated and contained 1 M *tert*-butyl alcohol in addition to Me_2S. DMSO formation from $^•OOCH_2CMe_2OH$ seems to occur only via the 2e process.

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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

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

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]

Acknowledgment. The financial support provided by the Association of International Cancer Research (AICR) is gratefully acknowledged.

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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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