Table I. Yield of Cyclohexanol in Polymer-Catalyzed Oxidations[a]

	polymer[b]	% yield of cyclohexanol + cyclohexanone	alcohol/ ketone
1.	F_{20} TPP–S–	70	45
2.	F_{20}TPP–S(–C$_6$F$_4$–C$_6$F$_4$–)$_{10}$	78	52
3.	F_{20}TPP–S(–C$_6$F$_4$–S–C$_6$F$_4$–)$_{10}$	65	55
4.	F_{20}TPP–S(–C$_6$F$_4$–P(–C$_6$F$_4$–)(–C$_6$F$_4$–))$_5$	60	45
5.	$F_{20}Cl_8$TPP–S–	33	90
6.	Cl_{20}TPP–S–[c]	70	100

[a] Catalyst (4 mg), PFIB (9.4 mg), and cyclohexane (54 μL) in 0.5 mL of the mixed solvent were stirred 3 min and analyzed (see text). The formulas refer to the original metalloporphyrin used in the polymerization. [b] The fluorines are on the phenyl groups. [c] The chlorines are on the phenyl groups.[2]

Preparation of different copolymers and the use of other oxidants such as hydrogen peroxide and dioxygen are also being investigated.

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Registry No. 1, 135645-47-5; **1** pentachloro derivative, 135645-48-6; **2**, 135645-49-7; cyclohexane, 110-82-7; cyclohexanol, 108-93-0; cyclohexanone, 108-94-1; norbornene, 498-66-8; norbornene epoxide, 278-74-0.

Electron Transfer and Back Electron Transfer in Photoexcited Ion Pairs: Forward and Back Directions Have Different Maximum Rates

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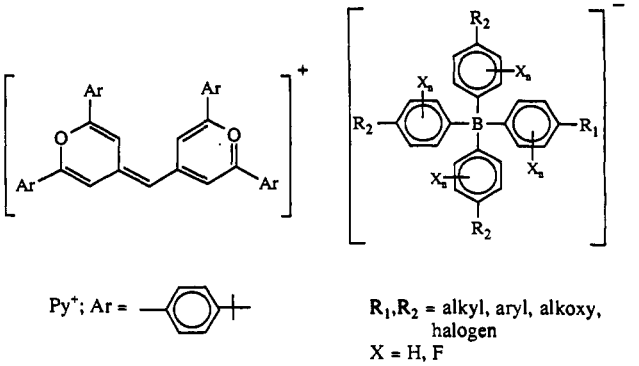
The efficiency of photoinitiated electron transfer in natural[1] and artificial[2] systems is determined by the competition between reaction rates. In the forward direction, transfer of an electron to or from an electronically excited state (k_{et}) competes with radiative and nonradiative dissipation of the excitation energy. In the back direction (k_{bet}), transfer of an electron to regenerate ground-state reagents competes with separation and irreversible chemical reaction. Current theoretical models recognize three key rate-determining parameters:[4-6] the driving force for reaction (ΔG_{et}), the reorganization energy (λ), and a measure of the electron-exchange interaction between donor and acceptor (V_r).

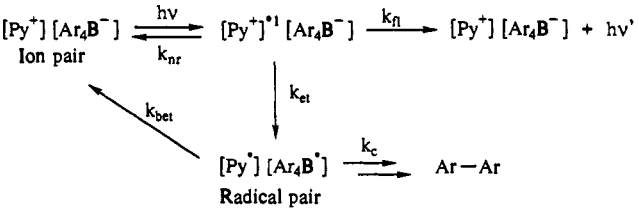
Herein we report results from investigation of photoinitiated electron transfer reactions in pyrylium borate ion pairs ([Py$^+$][Ar$_4$B$^-$], Chart I).[7,8] Systematic structural variation of the borate anion permits precise control of ΔG_{et} in both the forward and the back electron transfer. Ultrafast time-resolved spectroscopic measurements of k_{et} and k_{bet} reveal that V_r depends on the direction of electron transfer.

In benzene solution the pyrylium borate salts exist essentially exclusively as ion pairs.[8,9] However, since there is no or very little

Chart I



Scheme I



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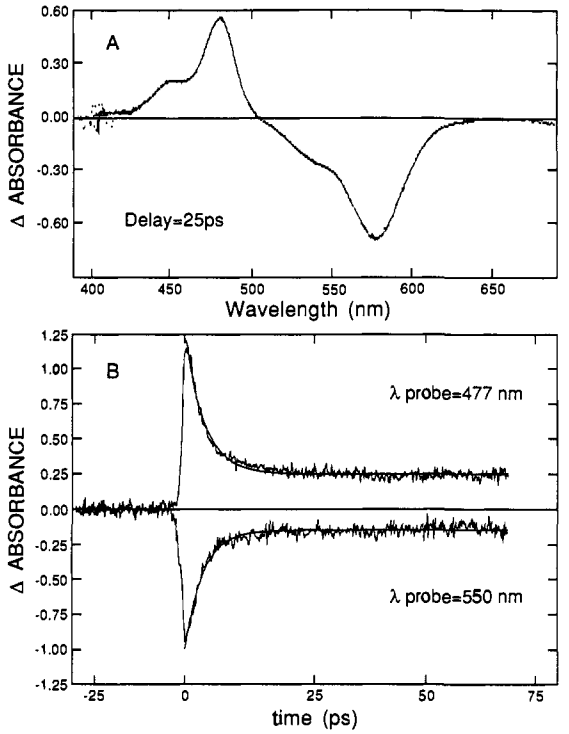

Figure 1. (A) Absorption spectrum recorded 25 ps after excitation of $[Py^+][n\text{-}BuBPh_3^-]$ in benzene solution at 532 nm with a 20-ps pulse. (B) Time-dependent change in absorptions following excitation of $[Py^+][(t\text{-}BuPh)_4B^-]$ in benzene solution at 573 nm with a 150-fs pulse. The upper curve shows the decay of the $[Py^\cdot]$ absorption, and the lower curve shows the recovery of $[Py^+]$ absorption. The residual $[Py^\cdot]$ and bleaching of $[Py^+]$ is attributed to irreversible reaction of $[(t\text{-}BuPh)_4B^\cdot]$: rate constant k_c.

dependence of their absorption or emission spectra on the identity of the borate, we conclude that electronic interaction between the ions is weak[10] and that excitation of $[Py^+]$ leads to the locally excited singlet state $[Py^+]^{*1}$. Three reactions are available to $[Py^+]^{*1}$ in the ion pair: fluorescence (k_{fl}), nonradiative relaxation to the ground state (k_{nr}), and forward electron transfer (k_{et}) to generate the radical pair $[Py^\cdot][Ar_4B^\cdot]$. Similarly, the radical pair may undergo two reactions: back electron transfer (k_{bet}), to regenerate the ground-state ion pair, and an aryl group coupling reaction (k_c), which in the case of tetraphenylborate leads to biphenyl.[11] These processes are summarized in Scheme I.

Electron transfer from $[Ar_4B^-]$ to $[Py^+]^{*1}$ in the ion pair is thermodynamically favorable in all cases examined except for that of $[(C_6F_5)_4B^-]$. The reduction potential (E_{red}) of $[Py^+]$ in CH_3CN solution is −0.60 V vs SCE, and its singlet energy (ΔE^{*1}) is 2.2 eV. Electrochemical oxidation of borates gives irreversible waves, so these potentials (E_{ox}) were estimated by the kinetic method described previously.[8,12] The free energy change for electron transfer from $[Ar_4B^-]$ to $[Py^+]^{*1}$ in the ion pair (ΔG_{et}) can be determined from eq 1, where W_p and W_r are Coulombic work terms for the ion and radical pairs, and E_{ox} and E_{red} are corrected for the change of solvent.[13] Energy conservation requires that $\Delta G_{bet} = -(\Delta E^{*1} + \Delta G_{et})$.

The lifetime of $[Py^+]^{*1}$ in the ion pair (τ_{Py}) is controlled by k_{fl}, k_{nr}, and k_{et} as is shown in eq 2. For $[Py^+]^{*1}[(C_6F_5)_4B^-]$, τ_{PyBF} is 40 ± 1 ps, measured by monitoring either the exponential

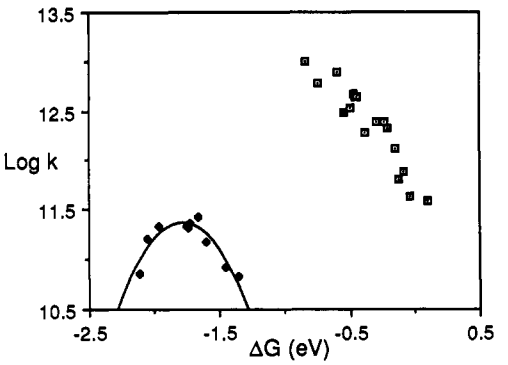

Figure 2. Marcus plots for electron transfer (□) and back electron transfer (◆) for the pyrylium borates in benzene solution. The free energy change for the reaction (ordinate) is based on empirical estimation of E_{ox} according to the Weller equation. The line shown through the back electron transfer data is the best fit to a parabolic equation.

recovery of its ground state (550 nm) or the decay of the $S_1 \rightarrow S_n$ absorption (470 nm) following pulsed laser excitation (150 fs, 573 nm, 5 μJ). Since k_{nr} and k_{fl} are presumed to be independent of the specific borate anion, and electron transfer cannot occur for $[(C_6F_5)_4B^-]$, k_{et} for the other pyrylium borates may be obtained from comparison of their fluorescence quantum yields (Φ_{PyB}) with that of $[Py^+][(C_6F_5)_4B^-]$ ($\Phi_{PyBF} = 0.006$) according to eq 3.

$$\Delta G_{et} = E_{ox} - E_{red} - \Delta E^{*1} - (W_p - W_r) \quad (1)$$

$$\tau_{Py} = 1/(k_{fl} + k_{nr} + k_{et}) \quad (2)$$

$$k_{et} = (1/\tau_{PyBF})[(\phi_{PyBF}/\phi_{PyB}) - 1] \quad (3)$$

Pulsed irradiation of $[Py^+][n\text{-}BuB(Ph)_3^-]$ yields a difference spectrum recorded 25 ps after excitation (Figure 1A) that shows bleaching of $[Py^+]$ and new absorptions at 455 and 477 nm assigned to $[Py^\cdot]$. Electron transfer is irreversible for $[n\text{-}BuB(Ph)_3^-]$ since carbon–boron bond cleavage to generate $(Ph)_3B$ and $[n\text{-}Bu]^\cdot$ is faster than back electron transfer. For tetraarylborates, back electron transfer competes with chemical reaction so both k_{bet} and k_c can be measured by monitoring either the decay rates of the $[Py^\cdot]$ absorption or recovery of the dye absorption (Figure 1B). Plots of k_{et} and k_{bet} against ΔG (Figure 2) clearly show Marcus inverted region behavior for back electron transfer but not for the forward direction.

Miller and co-workers formulate the rate constant for electron transfer as proportional to the product of $\langle V_r \rangle^2$ and the Franck–Condon weighted density of states (FCWD).[4a,14] The latter term yields the strong dependence of ΔG_{et} and contains the internal (λ_i) and solvent (λ_s) reorganization energies. Despite capability to measure k_{et} up to 10^{13} s^{-1}, there is no evidence that the maximum forward rate has been reached for the pyrylium borates. Conversely, k_{bet} has a maximum value of 2.7×10^{11} s^{-1}.

We expect that λ for k_{et} and k_{bet} will be nearly equal. In benzene solutions λ_s is negligible[15] and the change in dipole moment on excitation of the dye is small.[16] The largest contribution to λ_i comes from the significant change in carbon–boron bond order[17] and will be independent of the electron transfer direction. The magnitude of V_r is determined by the coupling of donor and acceptor orbitals and falls off exponentially from contact at distance r_o. Coulombic attraction assures close contact between pyrylium and borate in the ion pair, and a significant increase in separation within the lifetime of the radical pair is possible but seems unlikely.[18] Thus it appears that the difference in maximum

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value for k_{el} and k_{bel} is due to a change in interacting orbitals at r_o.

Electron transfer and back electron transfer involve different pyrylium orbitals. In the forward direction an electron from the carbon–boron bond is donated to the half-filled pyrylium HOMO, while in the back direction an electron from the pyrylium LUMO is transferred to the boranyl radical. We suggest that the aryl groups mediate electron transfer by superexchange similar to the way that bridging ligands appear to operate in bimetallic systems.[19] Thus strong overlap with the pyrylium HOMO enables a fast rate for the forward direction, but for the reverse, a weaker interaction between the LUMO and the occupied orbitals of the aryl groups leads to a diminished maximum rate.

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Supplementary Material Available: A table containing a list of the borates used and the electrochemical, spectroscopic, and kinetic data (1 page). Ordering information is given on any current masthead page.

(18) Crude estimates based on a classical mechanics model indicate a maximum acceleration of 0.1 Å/ps^2 and damping by viscous resistance of the solvent in a few picoseconds. Also, k_{bet} is unaffected by changing the solvent from benzene (η = 0.65 cP) to *p*-cymene (η = 3.4 cP).

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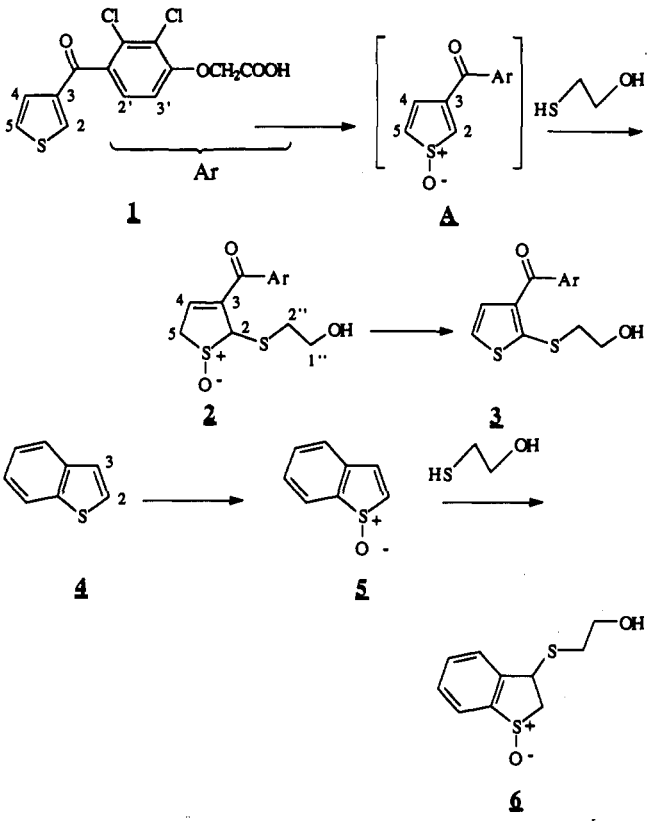
Scheme I



Thiophene *S*-Oxides as New Reactive Metabolites: Formation by Cytochrome P450 Dependent Oxidation and Reaction with Nucleophiles

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Although there is evidence that several thiophene derivatives cause toxic effects,[1] very little is known not only on the molecular mechanism of these effects but also, in a more general manner, on the oxidative metabolism of the thiophene ring.[2] Recently, it has been shown that the hepatic cytochrome P450 dependent oxidation of a diuretic drug, tienilic acid, and of its isomer with the arylcarbonyl group on position 3 of the thiophene ring, **1**, led to the formation of electrophilic metabolites that covalently bind to hepatic proteins[3] but the nature of which remained unknown.

In an effort to determine the nature of these electrophilic metabolites, we have undertaken the study of the metabolism of thiophene compounds by rat liver microsomes in the presence of a thiol-containing trapping agent.

This communication describes the initial results concerning the study of **1** and of a simpler thiophene derivative **4**. They provide initial evidence for the formation of thiophene *S*-oxides as reactive metabolites of thiophene-containing compounds and for the easy reaction of these reactive metabolites with nucleophiles.

As reported previously,[3a] oxidation of **1** by rat liver microsomes, in the presence of NADPH, led to metabolites most of which (70%) covalently bound to microsomal proteins, some unknown minor metabolites (30%) being detected by HPLC. Incubations under identical conditions but in the presence of nucleophiles like glutathione or mercaptoethanol led to a dramatic decrease of this covalent binding to proteins[3a] and to a concomitant appearance of new metabolites detected by HPLC. In the presence of 100 μM mercaptoethanol, only one major new metabolite, **2**, appeared. Despite its reactivity [i.e., **2** was rapidly and quantitatively transformed into a new compound, **3**, in acidic conditions (pH ≈ 1), and into other metabolites in the presence of excess mercaptoethanol] metabolite **2** could be isolated by preparative HPLC at neutral pH.[4] The UV, mass ([M + 1]$^+$ = 407), and ^{1}H NMR[5] spectra (Table I) of **3** clearly showed that it was derived from **1** by introduction of the S(CH$_2$)$_2$OH moiety at position 2 (Scheme I). The structure indicated for **2** was based on (i) its very characteristic ^{1}H NMR spectrum, with only one vinylic proton coupled to two geminal protons (H_5), a singlet at 5.44 ppm for H_2, two sets of signals corresponding to the SCH$_2$CH$_2$O moiety, and the signals of the Ar group almost identical with those of **3** (Table I); (ii) its UV spectrum, which was pH-dependent and exhibited bands as expected for a conjugated ketone at low pH and for a highly conjugated anion at high pH (pK ≈ 8.5); (iii)

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