of C_2H_4 renders the rhodium center more electrophilic, which favors a bridging M- - -H- - -C interaction.

Experimental Section

General Information. All complexes were manipulated under an atmosphere of dry, oxygen-free nitrogen within a Vacuum Atmospheres drybox or using standard Schlenk technique. Solvents were dried and degassed prior to use. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer. $C_5Me_5Co(CH_2CH_2)_2$, $C_5Me_5Rh(CH_2CH_2)_2$, and $C_5H_5Co(CH_2CH_2)_2$ were prepared by published procedures.[21-23]

Generation and NMR Characterization of Complexes 4a, 4b, and 6. **$Co(C_5Me_5)(CH_2CH_2)(CH_2CH_2\text{-}\mu\text{-}H)^+BF_4^-$ (4a).** $C_5Me_5Co(CH_2CH_2)_2$ (30 mg, 0.12 mmol) was dissolved in 5 mL of diethyl ether, and the solution was cooled to −30 °C. $HBF_4{\cdot}Me_2O$ (0.156 mmol) dissolved in 2.0 mL of ethyl ether was slowly syringed into the ether solution of the cobalt complex. $C_5Me_5Co(CH_2CH_2)(CH_2CH_2\text{-}\mu\text{-}H)^+BF_4^-$ began immediately to precipitate from solution. The solution was cooled to −78 °C and allowed to stand for 15 min to ensure complete precipitation. The ether was decanted from the precipitate, and the precipitate was washed with two 5-mL portions of cold ether. The precipitate was dried under vacuum at −30 °C, cooled to −78 °C, and dissolved in 0.8 mL of CD_2Cl_2. The solution was transferred by cannula to a precooled (−78 °C) 5-mm NMR tube equipped with a side arm and blanketed by nitrogen. The sample was sealed under vacuum at liquid nitrogen temperatures. The NMR tube was warmed to −78 °C prior to introduction into a precooled (−80 °C) NMR probe. ^{13}C NMR (−80 °C, CD_2Cl_2) δ 27.8 (td, J_{CH} = 151, 33 Hz, C_β,C_β'), 51.0 (t, J_{CH} = 150 Hz, C_α,C_α'), 100.0 (s, C_5Me_5), 9.0 (q, J_{CH} = 128 Hz, C_5Me_5). The ^1H NMR spectrum matches that previously reported.[8]

$Co(C_5H_5)(CH_2CH_2)(CH_2CH_2\text{-}\mu\text{-}H)^+BF_4^-$ (4b). NMR samples of **4b** were prepared as for **4a** using 30 mg (0.17 mmol) of $C_5H_5Co(CH_2CH_2)_2$ and 1.3 equiv (0.21 mmol) of $HBF_4{\cdot}Me_2O$. ^{13}C NMR (−90 °C, CD_2Cl_2) δ 23.6 (td, J_{CH} = 154 Hz, 27 Hz, C_β,C_β'), 48.2 (t, J_{CH} = 164 Hz, C_α,C_α'), 89.2 (d, J_{CH} = 185 Hz, C_5H_5).

$Rh(C_5Me_5)(CH_2CH_2)(CH_2CH_2\text{-}\mu\text{-}H)^+BF_4^-$ (6). The NMR sample was prepared as for **4a** using 30 mg (0.10 mmol) of $Rh(C_5Me_5)(CH_2CH_2)_2$ and 1.3 equiv (0.13 mmol) of $HBF_4{\cdot}Me_2O$. The following variations in sample preparation were used. The extraction of the salt with CD_2Cl_2 was performed with 0.4 mL of CD_2Cl_2 for the preparation of **6**. Me_2O (0.4 mL) was condensed into the NMR tube (−78 °C) and mixed with 0.4 mL of the CD_2Cl_2 solution of the cationic rhodium complex prior to sealing the sample. The Me_2O lowered the solution freezing point to ca. −135 °C. ^1H NMR (−110 °C, CD_2Cl_2) δ −8.6 (br, s, H_a), 1.38 (m, H_1,H_1' or H_2,H_2'), 1.85 (m, H_2,H_2' or H_1,H_1'), 2.56 (m, H_3,H_3' or H_4,H_4'), 2.73 (m, H_4,H_4' or H_3,H_3'), 1.75 (s, C_5Me_5). ^{13}C NMR (−129 °C, CD_2Cl_2/Me_2O) δ 8.5 (q, J_{CH} = 128 Hz, C_5Me_5), 103.5 (s, C_5Me_5), 52.0 (dt, J_{CH} = 160 Hz, J_{RhC} = 11 Hz, C_α,C_α'), 31.0 (ddt, J_{CH} = 153, 30 Hz, J_{RhC} = 5 Hz, C_β,C_β').

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Photochemical Generation of Radical Cations from α-Terthienyl and Related Thiophenes: Kinetic Behavior and Magnetic Field Effects on Radical-Ion Pairs in Micellar Solution[1]

Christopher H. Evans[2a] and J. C. Scaiano*[2a,b]

Contribution from the Ottawa-Carleton Chemistry Institute, University of Ottawa, Ottawa, Canada K1N 6N5, and Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. *Received June 6, 1989*

Abstract: The photochemistry of α-terthienyl (αT) and related compounds has been examined in homogeneous solution and in anionic micelles in the presence of electron acceptors. The absorption spectra of the radical cations from four thiophenic substrates have been characterized; for example, those derived from α-bithienyl (αB) and αT show absorption maxima at 420 and 530 nm, respectively. Triplet quenching by acceptors such as methyl viologen (MV^{2+}) and tetracyanoethylene approaches diffusion control ($k > 5 \times 10^9$ M^{-1} s^{-1}). Quenching by oxygen, which is known to be dominated by singlet oxygen sensitization, involves electron transfer only to a minor extent; the highest efficiency, for αB, was only 6%. In micellar systems the behavior of the radical-ion pairs produced via electron transfer involves the competition of geminate and exit processes which occurs in the 10^{-7}–10^{-6} s time domain. Both processes are slower in the larger micelles. Geminate processes are dramatically affected by magnetic fields. A model is proposed where the rate of geminate processes is suggested to depend upon the intramicellar reencounter frequency for the pair and the degree of singlet character in the triplet-derived radical-ion pair. The magnetic field effects observed are consistent with such a model.

α-Terthienyl (αT) and structurally related compounds are secondary plant metabolites[3] which are the subject of considerable interest because of their phototoxicity and possible insecticidal applications.[4-6] It is now well established that the lowest triplet states of αT and its analogues are excellent singlet oxygen sensitizers,[6,7] and their energy-transfer properties have been studied in considerable detail.[7c,f,8] It is now believed that the phototoxicity of αT in vivo is a direct result of αT's ability to generate singlet oxygen.[7f,9]

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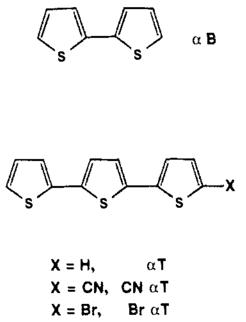
Chart I



In contrast, little is known about the electron donor/acceptor behavior of excited thiophenes. Preliminary results indicate that thiophene triplets (e.g., αT) are excellent electron donors but poor acceptors.[7f,8] In addition, ground-state thiophenes form weak charge transfer complexes with some electron acceptors[10] and can be electrochemically polymerized to form highly conducting electrochromic films of polythiophenes;[11-13] the proposed initiator in these polymerizations is the radical cation from the parent thiophene.[14,15]

We have recently reported the optical detection of the αT radical cation, $\alpha T^{\bullet +}$, formed in the photoreaction of αT with electron acceptors such as methyl viologen (MV^{2+}) or tetracyanoethylene (TCNE).[16]

It is now well established that the behavior of geminate triplet-derived radical pairs in micellar solution can be drastically modified by application of moderate magnetic fields.[17] For example, several neutral radical pairs have been examined in some detail.[18-21] Much less attention has been focussed on magnetic field effects involving micellized radical-ion pairs, with only a handful of reports addressing this topic.[22]

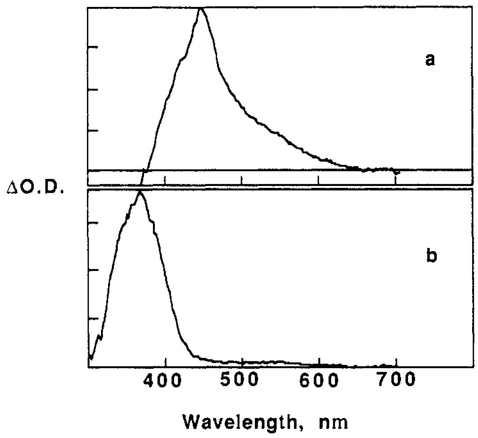


Figure 1. Triplet–triplet absorption spectra of 50 μM αT (a) and 0.6 mM αB (b) recorded in nitrogen-saturated acetonitrile 500 and 100 ns after the laser pulse and at 24 and 100% of full laser dose, respectively. Top ΔOD = 0.19 (a) and 0.29 (b).

The origin of magnetic field effects at moderate fields (≤5000 G in our case) is generally attributed to Zeeman splitting of the triplet sublevels which modifies the energy gap with the singlet state of the radical pair.[17] This mechanism usually leads to a slow down and eventual shut off of intersystem crossing (ISC) channels from T_+ and T_-, while T_0 remains unaffected.

This paper reports the results of a study of the photoinduced electron transfer behavior of αT and three related thiophenes (see Chart I) in both homogeneous and micellar solutions. For the latter, we have employed two anionic surfactants of different chain lengths. The electron acceptors used were methyl viologen, tetracyanoethylene and oxygen in homogeneous solution and methyl viologen in the micellar systems.

Experimental Section

The structures of the thiophenes studied and their abbreviations are given in Chart I. The bromo and cyano derivatives were a generous gift from Professor P. Morand; the details of their synthesis have been reported elsewhere.[7f,23] They were >99% pure by HPLC. The samples of 2,2′-bithienyl (αB from aldrich) and α-terthienyl (αT) were >99.5% pure, based on capillary GC.

Methyl viologen (MV^{2+}), obtained as the hydrated dichloride, and tetracyanoethylene (TCNE) were Aldrich products. Methyl viologen was recrystallized twice from ethanol, while TCNE was used as received. Sodium dodecylsulfate (SDS), "specially pure" grade from BDH, was used as received and sodium octyl sulfate (SOS) from Lancaster Synthesis was recrystallized from ethanol. The solvents were of the highest purity commercially available (Aldrich or Fischer spectrograde) and were used as received. Water was of conductivity grade (resistance ≥18 MΩ/cm^2).

Sample solutions used in laser flash photolysis experiments were prepared in cells constructed of 7 × 7 mm^2 Suprasil tubing, typically holding 2 mL. Solutions were deaerated by bubbling with oxygen-free nitrogen; we note that some of the very long triplet lifetimes recorded in this work may occasionally have been limited by the inability to remove the last traces of oxygen employing this technique. Thiophene concentrations were typically 20 μM for quenching studies and 100 μM for radical ion spectra, decay kinetics, and magnetic field studies. Concentrations of MV^{2+} or TCNE never exceeded 5 mM in homogeneous solution, but it was necessary to employ concentrations of up to 0.04 M MV^{2+} in micellar systems to compensate for the decrease in quenching efficiency resulting from compartmentalization and reduced mobility (vide infra). Under these conditions <20% of the laser light absorbed was absorbed by MV^{2+}. While this did not seem to introduce error in the kinetic measurements on the radical ions, we have preferred to monitor the radical-ion pairs (vide infra) at the wavelengths for the thiophene radical cations.

The use of static samples (as opposed to a flow system) leads to only minor substrate depletion during the course of the laser experiments.

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Table I. Spectroscopic Data for the Triplet States and Radical Cations from Thiophenes, and Efficiencies of Electron Transfer to Oxygen in Acetonitrile

substrate	$\lambda_{\max}^{TT\,a}$	$\lambda_{\max}^{\text{cation}\,a}$	$\lambda_{\text{isosbestic}}{}^{a}$	$\psi_{RC}{}^{b}$
αT	450[d]	530	500	≤0.01[c]
CNαT	493[e]	536	523	0.03
BrαT	465[e]	550	523	0.04
αB	370	420, 580	405	0.06

[a] In nanometers. [b] Measured at the isobestic point; see text. [c] From ref 16. [d] From ref 8; in methanol. [e] From ref 7f; in methanol.

Photoconversion of thiophenes was <10%, suggesting that irreversible photoprocesses occur with very low quantum yields. This was judged by UV spectroscopy; the spectra were recorded in a Hewlett-Packard 8451 diode array spectrometer.

The samples were irradiated at room temperature with the pulses (337.1 nm, ~8 ns, ≤10 mJ/pulse) from a Molectron UV-24 nitrogen laser. The transient traces (100 or 400 points), initially captured by Tektronix R-7912 transient digitizer, were then transferred to a PDP11/23$^+$ computer that controlled the experiment and provided suitable storage, processing, and hardcopy facilities. Further details have been reported elsewhere.[24]

Transient absorption spectra were recorded with an EG&G Series III optical multichannel analyzer (OMA) equipped with a 20-ns gate which can be delayed in time from the end of the laser pulse up to 1 ms in 10-ns steps. The OMA was operated in conjunction with a Jarrel-Ash spectrograph equipped with a 600 grooves/in. grating blazed at 500 nm. The analysis beam for OMA studies was provided by a 150-W xenon lamp. A typical experiment involved the collection and averaging of 10–20 transient spectral traces with a suitable luminescence correction.

The magnetic field source was a "homemade" electromagnet with a power supply which allowed for continuous variation in field strength from ~20 G (the residual field when no current was applied) to 5.4 kG. For "zero-field" (in fact the earth's magnetic field) experiments, the magnet was removed from the vicinity of the sample holder. The field strength was calibrated with a gaussmeter which had been previously calibrated against the magnetic field of an ESR spectrometer. The sample holder, optical table, optical bench, and mounts used near the sample compartment were built of nonmagnetic materials.

Results

Triplet-State Characterization in Homogeneous Solution. The triplet state of αB is the only one of those listed in Chart I which had not been characterized in earlier work.[7e,f,8] Nitrogen laser excitation of αB in acetonitrile leads to the formation of an intense, long-lived absorption with $\lambda_{\max}$ at 370 nm. This transient is formed within the duration of the laser pulse and is readily quenched by oxygen (k_{O_2} = (2.1 ± 0.2) × 10^9 M^{-1} s^{-1}), but not by 1,3-octadiene (k_q ≪ 10^4 M^{-1} s^{-1}). The transient lifetime, extrapolated to zero laser dose, is 27 μs under our experimental conditions. We assign this intermediate to the lowest triplet state of αB. At high laser doses the decay of this species exhibits a substantial second-order contribution. This type of behavior is not uncommon and is attributable to triplet–triplet annihilation. The inefficiency of 1,3-octadiene quenching suggests that the triplet energy of αB is less than 58 kcal/mol, as expected.[8] Figure 1 shows the triplet spectra for αB and αT, and the corresponding values of $\lambda_{\max}$ have been included in Table I.

Formation and Characterization of Thiophene Radical Cations in Homogeneous Solution. The radical–cation from αT has been characterized in earlier work.[16] In this section we present similar information for CNαT, BrαT, and αB.

The triplet states of these thiophenes are readily quenched by good electron acceptors such as MV^{2+} and TCNE. The corresponding rate constants were obtained from the decay kinetics (k_{exptl}) of the triplet state as a function of the acceptor concentration according to eq 1, where k_0 is the reciprocal of the

$$k_{\text{exptl}} = k_0 + k_q[\text{quencher}] \qquad (1)$$

thiophene lifetime in the absence of quencher and k_q the bimolecular rate constant for quenching. In the case of MV^{2+} it was also possible to monitor the reaction by following the formation of the reduced form, $MV^{\bullet+}$, at either 603 and 398 nm.[25] Representative plots are shown in Figure 2 and the corresponding rate constants have been summarized in Table II. It should be noted that the rather short lifetimes indicated by the intercepts may incorporate some triplet–triplet annihilation in the absence of quenchers, as well as self-quenching, which is common in thiophene derivatives.[8] This does not affect the quenching rates derived from the slopes of these plots. The rate constants in Table II typically approach diffusion control. Reactions 2 and 3 show the processes responsible for the quenching, where T is used to represent any of the thiophenes in Chart I.

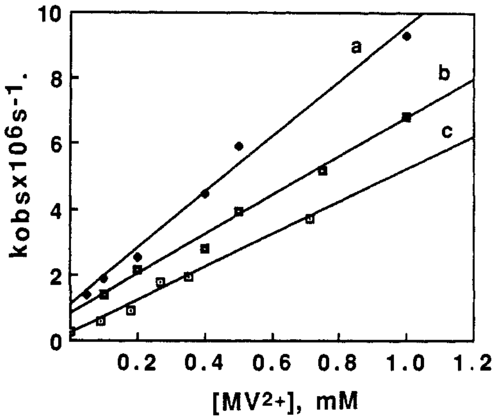

Figure 2. Quenching plots for the reaction of MV^{2+} with thiophene triplets in methanol: (a) αB, monitoring the growth of $MV^{\bullet+}$ at 603 nm; (b) BrαT, monitoring the growth of $MV^{\bullet+}$ at 603 nm; (c) CNαT, monitoring triplet decay at 420 nm.

Table II. Rate Constants for Quenching of Thiophene Triplets by Electron Acceptors

thiophene	acceptor	solvent	$10^{-9}k_q$,[a] M^{-1} s^{-1}	λ_{mon}, nm
αT	MV^{2+}	MeOH	6.8 ± 0.3[b]	450
	MV^{2+}	1:9 H_2O/CH_3CN	5.5 ± 0.4	450
	TCNE	CH_3CN	23 ± 6	650
αB	TCNE	CH_3CN	16 ± 4	425
	TCNE	CH_3CN	28 ± 4	600
	MV^{2+}	MeOH	8.5 ± 0.5	603
CNαT	MV^{2+}	MeOH	5.0 ± 0.6	420
BrαT	MV^{2+}	MeOH	5.9 ± 0.6	603
	TCNE	CH_3CN	16 ± 2	–

[a] Errors as ±2σ. [b] From ref 8.

$$^3T + TCNE \rightarrow T^{\bullet+} + TCNE^{\bullet-} \qquad (2)$$

$$^3T + MV^{2+} \rightarrow T^{\bullet+} + MV^{\bullet+} \qquad (3)$$

At concentrations of acceptor sufficient to quench over 90% of the triplets and at delays (following laser excitation) to allow for triplet decay, the spectra observed are those of the corresponding radical ions produced in reactions 2 or 3. These decay with second order kinetics, which we attribute to reverse electron transfer, e.g., in the MV^{2+} system (reaction 4).

$$MV^{\bullet+} + T^{\bullet+} \rightarrow MV^{2+} + T \qquad (4)$$

In the case of MV^{2+} as an acceptor, the signals from its reduced form, $MV^{\bullet+}$, are sufficiently intense that they can be readily observed in the presence of the various thiophene cations. In the case of TCNE as an acceptor the system is much cleaner and for practical purposes leads to readily detectable spectra of just the thiophene radical ions. The TCNE radical anion, $TCNE^{\bullet-}$, produced in reaction 2 has a relatively weak absorption in the spectral region of interest ($\lambda_{\max}$ 435 nm; ϵ_{435} = 7100 M^{-1} cm^{-1} in dichloromethane).[26] Only in the case of $\alpha B^{\bullet+}$ can we expect

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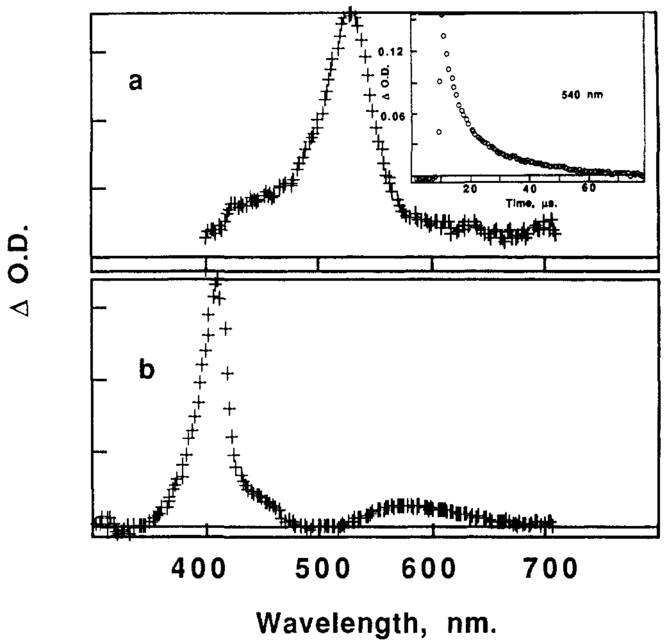

Figure 3. (a) Spectrum of CNαT radical cation recorded in the presence of 50 μM CNαT and 4 mM TCNE in nitrogen saturated acetonitrile 2 μs after the laser pulse. Top ΔOD = 0.11. The insert shows a decay trace for the same sample recorded at 540 nm. (b) Spectrum of the αB radical cation recorded in the presence of 100 μM αB and 12 mM TCNE in nitrogen saturated acetonitrile 120 ns after the laser pulse. Top ΔOD = 0.13.

some spectral interference (vide infra). The reader may note that the absorption mentioned above (for $TCNE^{\bullet-}$) is not really a "weak" one; however, it is in relative terms and in comparison with thiophene radical cations that this description applies. Figure 3 shows the spectra for $CN\alpha T^{\bullet+}$ and $\alpha B^{\bullet+}$ in acetonitrile. The spectra of the radical cation from the three trithiophenes ($\alpha T^{\bullet+}$, $Br\alpha T^{\bullet+}$, and $CN\alpha T^{\bullet+}$) are very similar. The corresponding λ_{max} values are shown in Table I. The spectrum of $\alpha B^{\bullet+}$ (Figure 3) show two bands (420 and 580 nm), which decay with identical kinetics and are therefore attributed to the same intermediate.

Figure 3 also includes as an insert the decay monitored at 540 nm for a sample of 50 μM CNαT and 4 mM TCNE in acetonitrile. The transient decays with second-order kinetics and a first half-life of ~15 μs. As in the case of $MV^{\bullet+}$, we attribute the decay to the back electron transfer, i.e. reaction 5.

$$T^{\bullet+} + TCNE^{\bullet-} \rightarrow T + TCNE \tag{5}$$

The fact that the decay of these intermediates can be largely attributed to back electron transfer is supported by the very low conversion (as judged by UV spectroscopy) observed on prolonged irradiation. In agreement with this observation, we find that the decay traces return to the preexcitation level, showing that no overall change in optical properties takes place. The same type of behavior has been reported earlier for the $\alpha T/MV^{2+}$ system.[8]

Table III lists values of $k_5/\epsilon_{T^{\bullet+}}$ for the reaction of various $T^{\bullet+}$ ions with $TCNE^{\bullet-}$ (reaction 5) in acetonitrile. The final values are all very similar and not unreasonable in view of the Coulombic attraction that will tend to favor the back reaction in the case of TCNE as an acceptor. The values of the extinction coefficients on which the rate constants (k_5) are based, are also included in Table III. Extinction coefficients were determined from transient spectra in deaerated $T-MV^{2+}$ systems. Under these conditions, bands due to both, $T^{\bullet+}$ and $MV^{\bullet+}$ are observed. Since the extinction coefficient for $MV^{\bullet+}$ is well known[25] and the degree of spectral overlap between $T^{\bullet+}$ and $MV^{\bullet+}$ is readily assessed, one can obtain the values for $T^{\bullet+}$.

Before closing this section, it is worth commenting on the possibility that ground-state complexes may be involved in the photoreactions studied. αB and TCNE are known to form a charge-transfer (CT) complex with λ_{max} 650 nm in acetonitrile.[10] However, the complex is a rather weak one, with an equilibrium constant for association, K_{CT}, of only 2.39 M^{-1}. Thus, under our experimental conditions ([αB] ~ 0.1 mM and [TCNE] ~ 12 mM) we would typically expect to form ~2.9 μM complex. Since the extinction coefficient at 650 nm is 660 M^{-1} cm^{-1}, we would expect an absorbance of ca. 1.3×10^{-3} in a cell with an 0.7-cm optical path. Such a small ground-state signal is not expected to introduce any interference in our measurements. Similarly, any interaction between T* and these complexes would occur with lifetimes >50 μs (even if diffusion controlled) and thus would have no effect on most of the studies reported herein.

Table III. Values of $k_5/\epsilon_{T^{\bullet+}}$ and $\epsilon_{T^{\bullet+}}$ Measured at 300 K in Acetonitrile

thiophene	$k_5/\epsilon_{T^{\bullet+}}$[b]	$\epsilon_{T^{\bullet+}}$,[c] M^{-1} cm^{-1}	$10^{-10}k_5$, M^{-1} s^{-1}
αT[a]	9.1×10^5	29000	2.6
αB	2.7×10^6	15900[d]	4.3
CNαT	9.1×10^5	59100	5.4
BrαT	1.5×10^6	42210	6.3

[a] Reference 16. [b] At $T^{\bullet+}$ λ_{max} in 0.7-cm path. [c] At $T^{\bullet+}$ λ_{max}. [d] May be subject to interference by $TCNE^{\bullet-}$. See text.

There seems to be no literature data on CT complexation between αT and TCNE, but the λ_{max} for the CT complex between TCNE and 2-methylthiophene is at 410 nm while that for the complex between TCNE and 5,5-dimethyl-2,2′-dithiophene is at 750 nm.[10] Although the effect of increased conjugation may not be as dramatic on going from a thiophene dimer to a trimer as it is on going from monomer to dimer, we suspect that any CT complex band in the αT/TCNE system may be at a long enough wavelength not to interfere in our measurements.

In the case of the $\alpha T/MV^{2+}$ system we examined the UV-vis spectra between 220 and 720 nm using 50 μM αT and concentrations of MV^{2+} of up to 44 mM in CH_3OH. The αT absorbance at 350 nm was not modified by addition of MV^{2+} and no new absorption bands were detected. Thus, our study does not provide any evidence for significant complexation between αT and MV^{2+} in the concentration range employed.

Oxygen Quenching of Triplet Thiophenes. We have recently reported that the quantum yield of superoxide formation in the oxygen quenching of $^3\alpha T$ in acetonitrile is very small, ≤0.01.[16] In spite of this low limit it was apparent that traces of $\alpha T^{\bullet+}$ were indeed formed. The general process that we attempted to monitor is illustrated in reaction 6, although the dominant process is of course energy transfer (reaction 7), leading to singlet oxygen.

$$^3T + O_2 \rightarrow T^{\bullet+} + O_2^{\bullet-} \tag{6}$$

$$^3T + O_2 \rightarrow T + {}^1O_2 \tag{7}$$

Since we had also observed that the decay kinetics of $\alpha T^{\bullet+}$ were insensitive to the presence of oxygen on our time scale (10 ns–200 μs), the extremely low yield of $\alpha T^{\bullet+}$ indicated that the superoxide route (reaction 6) was unimportant.

We have now extended the oxygen quenching experiments to include αB, BrαT, and CNαT. In all cases the decay of the radical cations in acetonitrile was largely insensitive to oxygen, showing that if $T^{\bullet+}$ is formed its detection should be straightforward. When the transient absorptions of these thiophenes (50 μM) were recorded in oxygen saturated acetonitrile (1 μs after excitation), the transient signals following triplet decay were very weak, supporting the fact that triplet quenching is dominated by energy transfer (reaction 7).

In spite of the low yield of reaction 6, it was clear that spectrum following triplet decay in the presence of oxygen, albeit weak, was that characteristic of $T^{\bullet+}$. The yields of $T^{\bullet+}$ were determined at the wavelength corresponding to the isosbestic point between the triplet and the cation, as in earlier work. This leads to a quantitative evaluation of the fraction of triplet quenching events that lead to $T^{\bullet+}$ (and therefore $O_2^{\bullet-}$) generation. These data (ψ_{RC}) have been included in Table I. While it is evident that electron transfer is a minor process in all cases, it is also clear that in some systems, αB in particular, it is not an insignificant process. In this system we also examined in detail the 700-nm region of the spectrum in deaerated samples. No evidence for solvated electrons

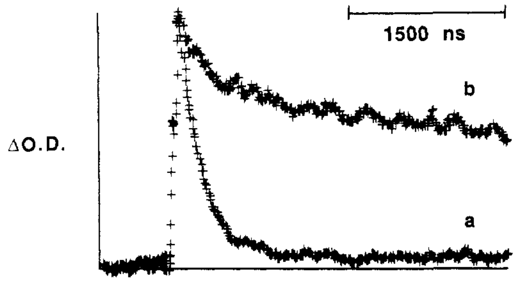

Figure 4. Decay traces recorded at 540 nm in the presence of 96 μM αT, 40 mM MV^{2+}, and 0.15 M SDS at zero (a) and 5 kG (b) applied magnetic field. The top ΔOD is 0.11 for both decay traces.

from αB was obtained, thus supporting the formation of $\alpha B^{\bullet+}$ via reaction 6, rather than direct photoionization.

Generation and Decay of Radical-Ion Pairs in Surfactant Solution. In fluid, homogeneous solution, geminate processes in a triplet-derived radical pair are both fast (frequently subnanosecond) and inefficient.[18c,27] Separation of the geminate pair is by far the dominant process. In surfactant solution the micelles act as microscopic cages;[17,18] under these conditions geminate processes requiring spin evolution and separation are competitive processes that occur in a much longer time scale, frequently hundreds of nanoseconds. In a geminate radical-ion pair the relative kinetics of reverse electron transfer and diffusive radical separation will determine the overall free radical yields of photochemical electron transfer reactions. Since direct reaction of a triplet radical pair to form closed shell products is spin forbidden, the yield of free radicals should be higher for triplet-derived radical pairs. For example, in the thionine/aniline system the radical-ion yield is 1.0 in homogeneous solution.[22e] It would therefore not be surprising if electron-transfer quenching of thiophene triplets also leads to high yields of free radicals in homogeneous solution.

Figure 4 shows decay traces (monitored at 540 nm) for a sample of 100 μM αT and 40 mM MV^{2+} in 0.15 M SDS at room temperature, measured in the absence and presence of a magnetic field (vide infra). The chromophore monitored under these conditions is largely the thiophene radical cation. While at 540 nm there is some contribution from $MV^{\bullet+}$, its contribution to the absorption does not exceed 30%. At any rate, since the decay observed can be attributed to back electron transfer in the $\alpha T^{\bullet+}/MV^{\bullet+}$ pair it makes no difference which radical ion (or mixture) is monitored. The transient spectra recorded are the same throughout the decay, including the residual absorption.

The zero-field trace of Figure 4 consists of two kinetic components, a rapid initial decay followed by a low intensity, long-lived residual absorption. As in other systems involving micellar reactions of radical pairs, we attribute the fraction of fast decay to geminate processes and the residual absorption to escape processes leading to the separation of the radical pair. Under these conditions the fast decay, which behaves monoexponentially, corresponds to the sum of rate constants for geminate and escape processes,[20] i.e. eq 8, where k_{gem} is the rate constant for geminate

$$k_{decay} = k_{gem} + k_{-} \tag{8}$$

decay and k_{-} is the sum of rate constants for all separation processes, usually involving the escape of each radical from the original micelle in which the geminate pair was generated. The fraction of escape, as determined by the ratio of residual absorption to the maximum absorption before significant decay takes place is given by[20]

$$\text{fraction of escape} = \frac{k_{-}}{k_{-} + k_{gem}} \tag{9}$$

Thus, from the experimental data it is possible to obtain k_{gem} and

Table IV. Geminate Reaction and Escape Data for Various Thiophene–Surfactant Combinations

				% exit	
surfactant	thiophene	$10^{-6}k_{gem}$, s^{-1}	$10^{-6}k_{-}$, s^{-1}	H = 0 kG	H = 5 kG
0.15 M SDS	αT	4.7	0.21	4.3	71
	CNαT	3.6	0.23	6.0	68
	BrαT	7.9	0.19	2.4	7.9
0.5 M SOS	αT	11.6	2.6	18	79
	CNαT	8.6	1.8	18	74

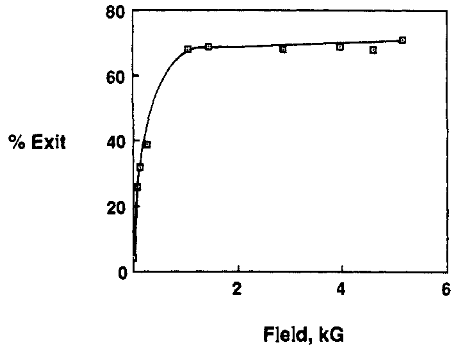

Figure 5. Variation in percent exit with magnetic field strength for the $\alpha T^{\bullet+}/MV^{\bullet+}$ radical-cation pair in 0.15 M SDS.

k_{-} from eqs 8 and 9. A summary of results is given in Table IV. For example, in the $\alpha T^{\bullet+}/MV^{\bullet+}$ pair only ca. 4% of the pairs undergo separation, suggesting that the highly charged negative micelle efficiently keeps the pair together for the time required for geminate processes to occur. We note that values of k_{-} based on such a small residual absorption (see Figure 4) may have a rather large relative error (as much as 50% for 5% escape), although this drops rapidly when the fraction of escape increases.

Application of magnetic fields leads to an increase in the residual absorption (and therefore escape) observed. Figure 5 illustrates the effect for the $\alpha T/MV^{2+}$ system; quite clearly the system reaches a plateau at fields over 1–2 kG. The field required to achieve one-half of the maximum effect ($H^{1/2}$) is only 130 G in this system. In this particular system escape increases from 4.3% at zero field to 71% at 5.2 kG. The yield of radical ions (as measured by the absorbance immediately following the laser pulse) was not affected by application of magnetic fields, indicating that the triplet state processes that precede radical formation are field independent.

We interpret the magnetic field effects as resulting from a slow-down of the processes by which the triplet radical pairs can access the singlet surface from the T_{+} and T_{-} triplet sublevels.[17-21] We further suggest (vide infra) that once a crossing to the singlet surface is achieved, the reaction proceeds rapidly to generate products and/or regenerate the starting materials. At intermediate fields (e.g., at $H^{1/2}$) the decay is complex and the fast component cannot be readily explained as a monoexponential component of the decay. This is an indication that interconversion among the various triplet sublevels in the $\alpha T/MV^{2+}$ system is slow in the time scale of the experiment.[20]

In order to carry out reliable kinetic studies in systems such as that illustrated in Figures 4 and 5, it is important to generate the radical ion pair in a time much shorter than its decay lifetime. This normally requires moderately high concentrations of electron acceptor. By contrast, at low concentrations (e.g., 2 mM MV^{2+} in the presence of αT/SDS) the formation of $\alpha T^{\bullet+}$ comprised two phases: a fast, "instantaneous" component followed by a slow growth in the microsecond time scale; in addition, triplet αT could be detected several microseconds after excitation. This may be a reflection of the fact that for 0.15 M SDS and 2 mM MV^{2+}, 35% of the micelles would not have any MV^{2+} associated with them (assuming a Poisson distribution) even if all the methyl viologen was associated with the micelles. At higher MV^{2+} concentrations the appearance of $\alpha T^{\bullet+}$ became instantaneous in

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our time scale and the residual absorbance decreased from a value of 24% at 2.3 mM (largely due to αT triplet, not escape) to about 5% at 15 mM MV^{2+}. The latter value was essentially independent of further changes in the concentration of MV^{2+} up to the highest one tried, 40 mM. Under these conditions ([SDS] = 0.15 M) we can estimate that about 0.038 M MV^{2+} will be associated with the micellar pseudophase taking 2400 M^{-1} (vide infra) as the association constant, K_a, of MV^{2+} with SDS. On the basis of these values, we can safely assume that all triplet thiophenes will find one or more acceptors in the same micelle; we therefore attribute the "instantaneous" formation of $\alpha T^{\bullet+}$ (or $T^{\bullet+}$ in general) to the efficient quenching of the triplet at high acceptor concentrations.

The value of K_a for MV^{2+} quoted above is the average of several literature values ranging between 844 and 4590 M^{-1},[28a–c] although a value of 70 000 M^{-1} has also been reported.[28d] Except for the last one, these values seem rather low when one compares them to typical equilibrium constants for the association of dications such as Cu^{2+} (10 000–60 000 M^{-1}), Ni^{2+} (10 900 M^{-1}), or Pb^{2+} (27 700 M^{-1}) with SDS.[29] We therefore attempted to measure K_a for MV^{2+} using the method of Encinas and Lissi[30] with excited singlet pyrene as a probe. Briefly, the underlying principle of this technique is that the value of I_0/I_Q observed in a steady state fluorescence quenching experiment depends only on the mean occupation number of the quencher, n_Q, in the micellar pseudophase and that this relationship is independent of the mechanism or efficiency of quenching. In particular, Stern–Volmer plots for the quenching of excited pyrene (λ_{ex} = 340 nm) by MV^{2+} were determined at several concentrations of SDS. The values of the concentration of MV^{2+} required to give the same value of I_0/I_Q at each micelle concentration were determined by taking horizontal "cuts" through the Stern–Volmer plots. These quencher concentrations were then plotted against micelle concentration for the various I_0/I_Q selected according to eq 10. [MV^{2+}] is the bulk viologen concentration needed to give a particular value of I_0/I_Q at the micelle concentration, [Mic].

$$[MV^{2+}] = n_Q/K_a + n_Q[\mathrm{Mic}] \qquad (10)$$

The usefulness of this method is rather limited in the two extreme cases where K_a is very small (quencher is fully dissolved in the aqueous phase) or very large (quencher is fully associated with the micellar environment). In the former case the observed quenching behavior will be independent of micelle concentration while in the latter case increasing the concentration of a Mic merely dilutes the fully micellized quencher. When this condition holds I_0/I_Q should be directly proportional to the concentration of Mic. At either of these two extremes the technique will not provide accurate quantitative results but will indicate that the quencher is strongly associated with one phase or the other.

For the MV^{2+}/SDS system with pyrene as a probe we have determined values of K_a ranging between 9000 and 14 000 M^{-1} and that I_0/I_Q varied essentially linearly with the concentration of Mic. A plot of I_0/I_Q vs [Mic] at fixed [MV^{2+}] gave a straight line (r^2 = 0.982) with a slope of 0.78 ± 0.16. The results should be interpreted to mean that MV^{2+} is quantitatively associated with SDS although these K_a values cannot be regarded as accurate. Nonetheless, our results suggest that the value reported by Atherton et al.[28d] is probably the more accurate one. This finding is borne out by laser flash photolysis measurements of the exit rate constant for $MV^{\bullet+}$ described below.

The data in Table IV were obtained employing a double-exponential treatment of the data, which readily separates the fast and slow components, as already indicated in earlier work.[20c] Several experiments were also carried out in micelles of sodium octyl sulfate (SOC) and the results have also been included in Table IV.

Discussion

The long-lived triplet states of all the thiophenes studied are readily quenched by good electron acceptors such as MV^{2+} and TCNE. Quenching leads to the thiophene radical cations which show strong absorptions in the 530–550-nm region for trimer systems and at 420 nm for αB. In homogeneous solution the radical ions are generated efficiently and decay by essentially diffusion controlled disproportionation to regenerate the starting materials.

Analysis of the behavior of radical–ion pairs in micellar systems presents several interesting features and throws some light regarding the type of interactions that determine the kinetics of geminate processes.

It is worth noting that the values of k_- show a clear dependence with micellar size. Similar effects have been observed before in the case of neutral radicals, as well as in reverse micelles.[20,22c,31] The values of k_- incorporate the rate constants for all processes that lead to the separation of the radical-ion pair, and therefore the loss of its geminate character. In our case this means the sum of the exit rate constants for $MV^{\bullet+}$ and $T^{\bullet+}$. The fact that these values are rather small (see Table IV) in spite of the obvious hydrophilicity of these species is a reflection of the Coulombic interactions that tend to keep the cations associated with the anionic micelles. Interestingly, if we assume that k_- represents an upper limit for the exit rate constant for $MV^{\bullet+}$ and that the association rate constant is controlled by diffusion (i.e. $\sim 1 \times 10^{10}$ M^{-1} s^{-1} for diffusion in water), then the equilibrium constant for $MV^{\bullet+}$ association with an SDS micelle must exceed 50 000 M^{-1}. We find it unlikely that the association value for $MV^{\bullet+}$ would be so much higher than the value for MV^{2+} suggested in the literature, and are therefore inclined to believe that the highest value discussed above represents the best approximation for the true value. Such high values for the equilibrium constants simply mean that for practical purposes the MV^{2+} and $MV^{\bullet+}$ ions are quantitatively associated with the micelles in SDS surfactant solutions. This quantitative association may be in part responsible for the wide variation in K_a literature values. This would be particularly problematic in systems where K_a was estimated by MV^{2+} quenching of an extra micellar probe.[28a,b]

In the systems described herein the exit process probably does not involve migration from the oil phase to the water but rather release from the micellar surface and into the aqueous phase. The values are probably remarkable only in the large change observed in going from C_8 to C_{12} micelles.

We note that in addition to the exit rates, the rate constants for intramicellar quenching have also been reported to depend on micellar size.[29]

The analysis of the values of k_{gem} should be carried out in the light of our knowledge of the factors that control the lifetimes of flexible biradicals in solution.[32] A recent, extensive review on magnetic field effects also provides an analysis of the key elements for this discussion.[33] In a sense a micellized radical pair is simply a biradical where the distance between radical centers is controlled by the dimensions of a phase boundary, rather than by the structure of a molecular framework. In our examples we can reasonably assume that the radical-ion pair moves *on* the micellar surface rather than *in* the micelle. Two questions are critical. First, to what extent is diffusional motion (as opposed to spin evolution leading to intersystem crossing) an important factor in determining the rates of geminate processes in the absence of a magnetic field. Second, if spin evolution is important, what

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type of interactions determine the magnitude of k_{gem}. Most reports on the subject have generally assumed that k_{gem} is controlled by intersystem crossing;[17-20,21d,e,22b,d] however, a recent report by Turro et al.[34] has suggested that the rate constants for geminate decay of benzylic radicals in micelles in the absence of a field are partly determined by diffusional motion of the radicals within the micelle. All models agree that once a moderate field has been applied the reaction of $T_\pm$ pairs is controlled by spin evolution.[33] It should be noted that the numerous examples of isotope enrichment[34] cannot be explained by a diffusive-only mechanism; clearly other types of interaction must play a role even at zero field.

One may suggest that in the radical-ion pairs studied herein, their reactive decay, as measured by k_{gem}, could be controlled solely by intersystem crossing, not diffusive reencounters. In support of this, we note that the value of k_{gem} for BrαT is nearly twice as high as that for αT. It is hard to see how substitution by bromine could possibly enhance the rate of diffusion; in contrast, it is straightforward to associate heavy-atom substitution with an increase of the rate constant for triplet–singlet intersystem crossing. It is worth noting that a similar increase in the observed decay rate constant upon bromine substitution has been observed for biradicals containing benzyl radical centers.[35]

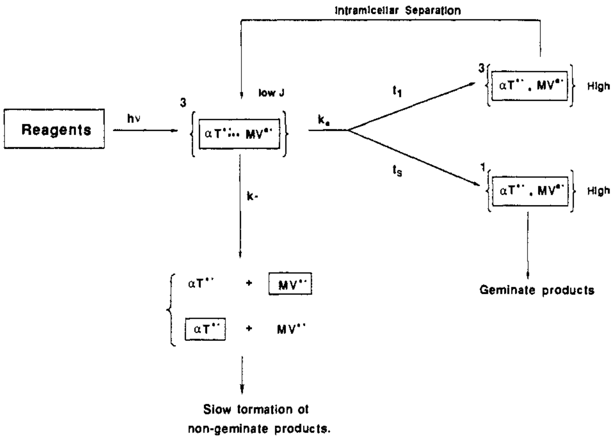
The values of k_{gem} are systematically higher for the smaller micelles. A similar effect has been observed in flexible biradicals.[36] If we make the reasonable assumption that the average distance between radical centers is larger in the larger micelles, then we could conclude that SO coupling plays a role in determining the lifetime of the radical pairs, since the inverse dependence of k_{gem} with distance is common in processes controlled by SO coupling, rather than by hyperfine interactions.[37-41] However, processes controlled by SO coupling are rather insensitive to magnetic field effects, in contrast with our experimental observations.

A purely diffusion controlled model would of course explain the size effect but would fail to account for some of our observations above (e.g., effect of bromine substitution). We suggest that trying to interpret the data on the basis of *either* a spin evolution *or* diffusional model is an oversimplification. When the radical centers can separate sufficiently to make the electronic exchange energy small compared to hyperfine coupling, the latter will cause mixing of the triplet and singlet spin states of the radical pair in the absence of applied fields.[33,42] Thus, a triplet-derived radical pair is better viewed as having predominantly triplet character, but with a certain degree of single character, f_s. Thus, in every radical reencounter f_s will determine the probability of crossing to the singlet surface and thus in an oversimplified view of "net intersystem crossing". Radical–radical reactions can only occur at short distances, since bond formation is always involved. Thus, we expect the intramicellar reencounter frequency (k_e) to be the other factor, in addition to f_s, to control k_{gem}, i.q., eq 11.

$$k_{gem} \propto k_e f_s \qquad (11)$$

k_e is related to the reciprocal of the micellar volume and to the mutual diffusion coefficient of the reactive species,[43,44] while f_s will probably become larger in the bigger micelles, where smaller exchange energies can be achieved through intramicellar separation. Thus, in our case we conclude that the size dependence of the experimental values of k_{gem} are largely dominated by the changes in k_e. The large magnetic field effects can be easily accommodated in this model, since an applied field will drastically reduce the efficiency of $T_\pm \leftrightarrow S$ mixing as the Zeeman splitting becomes large relative to hyperfine interactions.

Scheme I



Scheme I shows the mechanism proposed, where the rectangular boxes reflect micellar compartmentalization and the curly brackets emphasize the mixed character of the geminate radical pair spin states, even when the superscripts 3 and 1 indicate the dominant character. The extended dots (as in $\alpha T^{\bullet+}\cdots MV^{\bullet+}$) indicate a radical pair for which the intramicellar separation is sufficiently large for the exchange interaction, J, to be small.

The effect of magnetic fields on the yield of radicals that escape (see Table IV) is considerably smaller in the case of radical pairs containing heavy atoms; thus, application of a 5 kG field in the case of αT changes the escape yield from 4 to 71% (SDS micelles). By contrast, in the case of BrαT the yield changes from 2.4 to only 7.9%. The result is very unlikely to be related to changes in polarity of the thiophene donor, since the results for CNαT are virtually identical with those for αT. Similar heavy atom effects have been reported in other systems[18e,22e,g,h,45] and have been attributed to a change in mechanism from hyperfine coupling to SO coupling[18e,45] or to the increased contribution of spin–rotational relaxation to $T_\pm \rightarrow S$ (and $T_\pm \rightarrow T_0$) interconversion in the presence of heavy atoms.[22e] As indicated before, in the case of αT we believe the interconversion between triplet sublevels to be a slow process in the time scale of k_{gem}. If this condition is preserved in the presence of a field, we expect that at a sufficiently high field the $T_\pm \rightarrow S$ spin conversion channels will be shut off, while for T_0 the competition between escape and spin evolution will remain essentially unaffected. It is straightforward to estimate that for all the SDS systems in Table IV escape will saturate at about 70% if the conditions above are met. This is indeed true for αT and CNαT, but not for BrαT. We suggest that in the case of BrαT the criterion of slow interconversion between triplet sublevels is not met.

In the limit of fast interconversion of triplet sublevels the situation is quite different from that described in the previous paragraph. Here even if spin conversion from $T_\pm$ was completely shut off, these sublevels could still "leak" into the singlet manifold via conversion to the T_0 level. In the limit k_{gem} would be reduced to one-third (assuming equal T_+, T_-, and T_0 initial populations) of its value at zero magnetic field and therefore for BrαT the escape yield could go up to about 7%. When one takes into account that this only applies in the high field, fast sublevel interconversion limit, and that k_- carries considerable error, the

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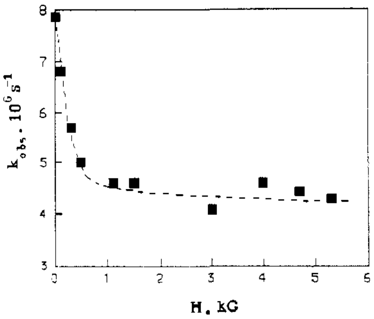

Figure 6. Plot of k_{obs} for BrαT$^{\bullet+}$/MV$^{\bullet+}$ pair in 0.15 M SDS as a function of field strength. [BrαT] = 100 μM, [MV^{2+}] = 40 mM.

value is entirely consistent with the escape yield of 7.9% observed experimentally.

To test the applicability of these considerations to the present system we fit the decay traces for the αT and BrαT system in SDS at zero field and at 5 kG applied field. In all cases a good fit was obtained as judged by the random distribution of weighted residuals. By assuming k_- to be field independent it was possible to calculate k_{gem} both at high and low fields. For αT these values are 4.7 × 10^6 s^{-1} at zero field and 4.0 × 10^6 s^{-1} at 5 kG while for BrαT k_{gem} was found to be 7.9 × 10^6 s^{-1} at zero field but only 4.3 × 10^6 s^{-1} at high field, i.e. about $^1/_2$ of the zero field value. These data strongly support our view of slow triplet sublevel interconversion in the case of αT and fast interconversion in the BrαT system.

It should be noted that for αT, the fact that k_{gem} is approximately the same at zero field and 5 kG does not mean that there is no magnetic field effect in this system, but rather that once the $T_\pm$ channels have been shut off the k_{gem} value (at 5 kG) only measures the process for T_0, which remains constant, as expected. With the k_{gem} route closed to $T_\pm$ these will undergo the exit process and contribute about 66% to this process; with a minor T_0 contribution, total exit will be around 70%.

What is the source of this rapid interconversion between triplet sublevels in the BrαT$^{\bullet+}$, MV$^{\bullet+}$ radical-ion pair? One possible explanation is similar to that offered by Ulrich and Steiner.[22c,e] These authors write the rate constant for spin relaxation mediated interconversion between spin states of the radical pair, k_{rel}, as in eq 12, where k_{AHF} is the anisotropic hyperfine coupling term, k_{SO}

$$k_{rel} = k_{AHF} + k_{SO} + k_{SR} \tag{12}$$

is the spin-orbit coupling term arising due to anisotropy of the g-factor, and k_{SR} is the spin-rotational coupling term. The former two rate constants are field dependent while the latter is not. As a result k_{rel} can never be smaller than k_{SR}. When k_{SR} is substantially larger than k_{gem} ($H = 0$), there will be rapid spin sublevel interconversion so that even at high fields $T_\pm$ will be able to "leak" into T_0. The magnetic field will then be less effective at inhibiting $T_\pm \rightarrow S$ spin conversion.

The magnitude of k_{SR} is related to the value of the longitudinal relaxation time, T_1, of the radical which is subject to increased spin-orbit coupling in the presence of a heavy atom (αT$^{\bullet+}$ in this case). Typical values of T_1^{-1} fall in the range of 10^4–10^6 s^{-1} for light atom radicals but may be substantially higher for radicals bearing heavy atoms.[46] Thus one would expect bromine substitution of the αT moiety to increase k_{SR}. Presumably the increase in the value of this rate constant is sufficient to make the rate of triplet sublevel interconversion at high field comparable to or greater than the rate of $T_0 \rightarrow S$ spin conversion. We believe that in our system the sublevel interconversion ($T_\pm \rightarrow T_0$) is fast compared to $T_\pm \rightarrow S$ spin evolution. In support of this, we note that a plot of k_{obs} (which for BrαT is largely determined by k_{gem}) vs the field strength (Figure 6) shows that the effect saturates at $\leq$1000 G. Thus, direct access to the singlet surface from $T_\pm$ is not important above 1000 G. Therefore, the small magnitude of the magnetic field effect in this system is due to the rapid $T_\pm \leftrightarrow T_0$ interconversion caused by the presence of a heavy atom.

Conclusions

We have presented data indicating that triplet thiophenes are excellent electron donors both in homogeneous and in micellar solutions. Electron transfer from triplet thiophenes to suitable electron acceptors leads to formation of the strongly absorbing, rather stable thiophene radical cations which in the ns-μs time scale are insensitive to the presence of oxygen. The main decay pathway of these radical cations in organic solvents appear to be almost quantitative, second-order, diffusion-controlled reaction back to the thiophene precursor.

Quenching of thiophene triplets by oxygen leads to only minor yields of the corresponding radical cations and therefore, by inference, to only minor yields of superoxide anion in vitro. This is consistent with the currently held view that thiophene phototoxicity is largely due to the ability of the triplet state of this class of compounds to sensitize singlet oxygen.

In micellar solution the radical cations formed via electron transfer from triplet thiophenes to methyl viologen dication decay by a first-order process after the completion of which there is a 5–10% residual absorption. The observed decay kinetics and the efficiency of this recombination process are quite sensitive to the strength of an applied magnetic field. This indicates that the intramicellar electron transfer results in the formation of a micellized triplet radical-cation pair. The exit rate constant for this pair seems to depend, at least qualitatively, on the micellar dimensions, with k_- being reduced in larger micelles. The rate constant for geminate recombination at zero field also correlates with micellar dimensions and is enhanced by substituting the thiophene moiety with bromine.

The dependence of k_{gem} on micellar dimensions, along with the increase in its value upon bromine substitution has led us to the conclusion that the value of k_{gem} is related to the product of the radical reencounter frequency and the degree of singlet character in the triplet-derived radical pair. Furthermore our comparison of k_{gem} at zero and high fields for the αT and BrαT systems suggests that while high field triplet sublevel interconversion must be slow for the former, it must be rapid for the latter. It may be that the differences between these two systems can be explained by enhanced spin-rotational relaxation in the bromine substituted case.

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