are promising first steps on the way to understanding the thermal evolution of alumina sol–gels en route to ceramic materials.

Acknowledgment. We thank the Ontario Centre for Materials Research for seed funding for this project (L. F.N.) and NSERC for support via a Strategic Grant and through operating grants (to L.F.N. and A.D.B.). We also thank Dr. Tim Allman for making NMR-286 available to us. We are grateful to Dr. Brian Sayer and Dr. Don Hugues at McMaster and Janet Venne at Waterloo for their technical NMR assistance.

Appendix

Integrated intensities of the ^{27}Al NMR resonances for selected GPC fractions are given in Table III.

Registry No. Al_2O_3, 1344-28-1; $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$, 12703-68-3.

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Photophysical and Photochemical Studies of Phenothiazine and Some Derivatives: Exploratory Studies of Novel Photosensitizers for Photoresist Technology[1,†]

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The photochemistry and photophysics of a series of phenothiazine derivatives have been examined by using a combination of time-resolved laser techniques. The triplet states, which are readily detectable by using laser flash photolysis techniques, decay with lifetimes in the neighborhood of 1 μs; these lifetimes are frequently influenced by self-quenching processes. All the phenothiazines are modest singlet oxygen sensitizers, with yields, Φ_Δ, in the 0.18–0.46 range. The rate constants for the reactions of both singlet and triplet states with bromo compounds correlate well with the free energy for electron transfer. Increased delocalization (e.g., by introduction of naphthalene moieties) shifts the ground-state spectrum to the red so that they show significant absorption at the mercury lamp g line; however, the rate constants for reaction with I (1,3,5-tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione) are reduced to a point where only singlet processes are likely to be of importance.

Introduction

A number of negative photoresist systems have been reported over the years that involve a variety of insolubilization schemes.[5,6] Photoinduced cross-linking of the matrix polymer is a mechanism often employed in order to achieve differential solubility. In these systems the cross-linker (which may be part of the polymer chain) can be inherently photoactive or it can be activated by another component of the resist. Typical examples include poly(vinylcinnamate) resists,[7] bisazide-based resists,[8] and acid-catalyzed cross-linking systems (e.g., epoxy materials).[9]

Recently, a family of acid-hardened photoresists has been developed. They are comprised of three components; a photosensitive acid generator (PAG), an acid-activated, thermally assisted cross-linker, and a phenolic polymer. The cross-linking chemistry of these systems is related to that found in thermoset coatings.[10] In the first step the resist is exposed and acid is liberated from the PAG. The acid in turn activates a multifunctional cross-linker, which upon heating reacts with the polymeric matrix according to Scheme I.

Two high-resolution negative resists for use with e-beam and deep-UV exposure tools have been reported.[11,12] In addition to having high contrast, these systems exhibit excellent plasma etch resistance and thermal stability.

For certain applications it is advantageous to extend the photosensitivities of all of the aforementioned systems to 365 (i line) and 436 nm (g line), the wavelengths used with conventional diazonaphthoquinone/novolak photoresists. To accomplish this, an appropriate chromophore may be incorporated into the structure of the PAG or, alternatively, by the addition of a photosensitizer capable of activating the PAG. Both of these approaches have been utilized with a variety of PAG molecules. The spectral sensitivity of onium salts has been shifted to longer wavelengths by adding extended aromatic substituents.[13] A wide variety of aromatic sensitizers have also been used in conjunction with onium salts in order to generate acid

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[†] Dedicated to Professor Kurt Schaffner on the occasion of his sixtieth birthday.

(1) Issued as NRCC-32326.
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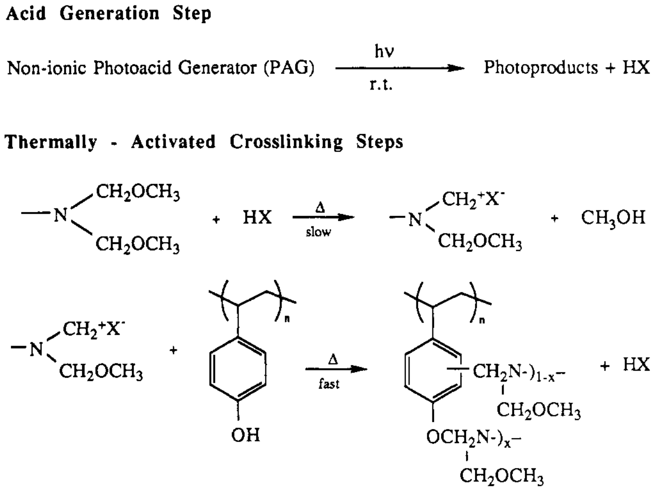
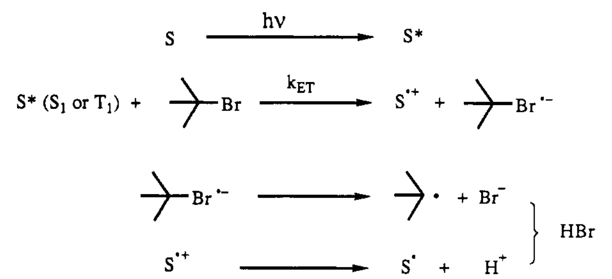
Scheme I



Scheme II

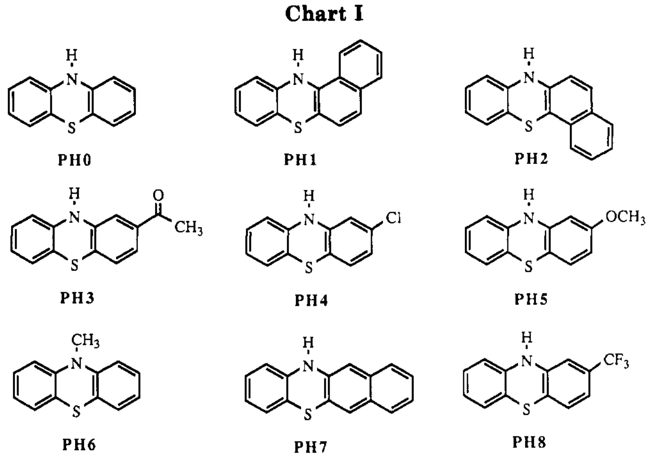


at longer wavelengths. The mechanism of sensitization in the latter case was shown to occur via electron transfer from the excited state of the sensitizer to the salt.[14,15]

The latter approach was utilized in this study to sensitize 1,3,5-tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (I), one example of a nonionic, bromine-containing PAG.

I has little optical absorbance above 300 nm. Phenothiazines were identified as possible sensitizer candidates for I since phenothiazine itself exhibits the ability to photoreduce alkyl halides with high efficiency.[16] Furthermore it has also been demonstrated that vicinal dibromides yield large amounts of halogen acid when appropriately sensitized in the presence of hydrogen donors.[17] The mechanism of sensitization for phenothiazines, when used in conjunction with bromine-containing compounds, is believed to be that of Scheme II. The acid generated from this sequence initiates the cross-linking reaction, which results in the insolubilization of the exposed areas of the resist.

Chart I



The present work was undertaken to gain insight into the mechanisms that determine the efficiency of those photosensitizers. For this purpose, we have employed laser flash photolysis techniques, luminescence spectroscopy, time-correlated single-photon counting, and optoacoustic spectroscopy. The results of the present study provide a framework for the understanding of the spectroscopic factors that determine the usefulness of phenothiazines in photoresist applications.

In the application of photoacoustic spectroscopy to these systems we have developed a new approach to the determination of intersystem crossing yields that may be applicable to many other systems.

Experimental Section

Materials: The phenothiazines used in this work and their abbreviations have been listed in Chart I. Compounds PH0, PH3, PH4, and PH8 were obtained from Aldrich. PH5 and PH6 were purchased from TCI and Kodak, respectively. The first group was recrystallized from toluene prior to use, and PH6 was recrystallized from ethanol. PH1 and PH2 were synthesized according to the literature[18] and recrystallized from toluene followed by purification on a silica plate using a 1:1 ethyl acetate:hexane mixture as eluant. PH7 was prepared by the method of Van Allan[19] followed by recrystallization from toluene. Electrometric grade [*n*-Bu$_4$N]BF$_4$ (Southwestern Analytical) was used as the supporting electrolyte for all electrochemical measurements. Diglyme (bis(2-methoxyethyl) ether) and compound I (1,3,5-tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione) were obtained from Aldrich and used without further purification. Acetonitrile (Omnisolv) and acetonitrile-d_3 (99.9% deuterated) were purchased from BDH and MSD Isotopes, respectively.

General techniques: Ground-state absorption spectra were recorded by using a Hewlett-Packard 8451A UV–visible diode array spectrophotometer. Steady-state fluorescence emission was recorded by a Perkin-Elmer LS-5 spectrofluorimeter equipped with a 3600 data station to control the experiment. Phosphorescence emission was recorded at 77 K by using the same device incorporating a liquid nitrogen Dewar. Time-resolved fluorescence studies utilized a PRA single-photon-counting apparatus with typical pulse duration of ca. 1.5 ns.

Redox properties: All electrochemical measurements were made using a BAS Model CV-1B cyclic voltammograph connected to a YEW Model 3022-A4 *XY* recorder. A Pt wire working electrode was used with a Pt gauze counter electrode. The reference electrode was a Ag/Ag$^+$ (a silver wire immersed in 0.1 M AgNO$_3$/CH$_3$CN from Koslow Scientific). The $E_{1/2}$ values as determined by cyclic voltammetry (the averages of the anodic and

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cathodic peaks for first oxidation wave only recorded at 100 mV/s by using ≈1 mM solutions of the compounds in CH_3CN containing 0.1 M [n-Bu_4N]BF_4) are used as the formal potentials, $E^{\circ\prime}$, which are reported in the tables. All values are vs Ag/Ag^+. Peak separations for the first oxidation waves for all phenothiazines were generally <90 mV, indicating a high degree of reversibility. Reduction of I is irreversible, and $E^{\circ\prime}$ is taken as the potential at half the wave height. Since the wave is irreversible, this represents only a minimum estimate of $E^{\circ\prime}$. Use of this value to calculate ΔE's would then yield minimum estimates of this value. Reduction of the phenothiazine derivatives is not observable in acetonitrile to ~−2.0 V vs Ag/Ag^+ (cathodic limit).

Laser flash photolysis: Laser experiments were carried out by using a Molectron UV-24 nitrogen laser (337.1 nm, ~8 ns, ≤10 mJ/pulse) for excitation. Static and flow sample cells were constructed of 3 × 7 mm^2 Suprasil tubing. The flow technique was preferred for spectral acquisition, given the large number of laser shots required and the relative photoinstability of the compounds, especially in the presence of electron acceptors such as I. Unless otherwise indicated, the samples were purged by nitrogen bubbling prior to irradiation. Transient spectra were recorded employing a point-by-point approach both in the absence and presence of I, which allowed the determination of both triplet and radical-cation spectra for the phenothiazines. The solvent of choice was diglyme, largely as a result of the excellent solubility of I in this solvent.

Self-quenching experiments were carried out on static samples employing a series of cells of variable optical path; these were constructed of 7 × 7 and 3 × 7 mm^2 Suprasil tubing or of 0.7 × 7 and 0.3 × 7 mm^2 Pyrex tubing.

Laser-induced optoacoustic calorimetry (LIOAC): Quantum yields of intersystem crossing (Φ_{isc}) were estimated by using LIOAC, as previously described,[20] and employing the attenuated 355-nm pulses from the third harmonic of a Lumonics Hyperyag-750 Nd:YAG laser for excitation. As the exact nature and efficiencies of the deactivation pathways for the excited phenothiazines were not explicitly known, a novel approach was developed to carry out these measurements. This is based on the following measurements:

(i) PHx was dissolved in solution to an absorbance of ~0.15 at the excitation wavelength of 355 nm and deoxygenated by bubbling with N_2 for 15 min, prior to irradiation. The dependence of the LIOAC signal on the incident laser energy was then measured.

(ii) A sample identical with that studied in (i) but containing 0.05 M 2,5-dimethyl-2,4-hexadiene, an efficient triplet quencher, was prepared, and the energy dependence measured.

(iii) The laser energy dependence of a reference solution of o-hydroxybenzophenone at the same absorbance and in the same solvent was then measured.

The latter solution (iii) deactivates rapidly and exclusively by nonradiative means and α, the fraction of the absorbed energy delivered back to the solution as heat within the detection time, is unity. The detection time (τ_D) under our conditions (laser beam diameter of 0.5 mm) is ~450 ns, as determined by the transducer response frequency of 2.25 MHz. α values for PHx solutions in cases (i) and (ii) are then obtained from direct comparison of the slopes of the energy dependence plots to the reference, (iii).

In case (i) we have the triplet state of PHx as an energy storing state ($\tau_T \sim 3.5\ \mu s$), but the missing energy $(1 - \alpha)$ may also contain contributions from radical and radical ion formation (vide infra), the extent and energetics of which are not known. In case (ii) the PHx triplet is exclusively quenched, by triplet energy transfer, to a lifetime of <40 ns by the diene which itself is short lived (τ_T = 44 ns)[21] such that all of the energy originally stored in the triplet state in (i) is now detected in (ii). Thus, the difference in α value between (i) and (ii) is directly that of the PHx triplet state, and it is apparent from energy balance considerations that

$$[\alpha(\text{ii}) - \alpha(\text{i})]E_L = \Phi_{isc}E_T \qquad (1)$$

where E_L is the laser energy of 80.7 kcal mol^{-1} (355 nm), and as the triplet energies have been obtained from phosphorescence measurements[22] the Φ_{isc} values may be evaluated from eq 1.

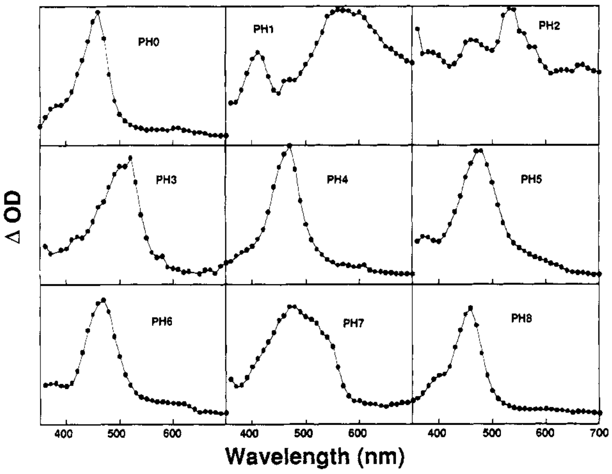

Figure 1. Triplet–triplet absorption spectra obtained within 200 ns of the excitation pulse for PH0 to PH8 in nitrogen-saturated diglyme.

It should be noted that in contrast to the normal application of LIOAC where the alternate deactivation modes to that of interest are usually quantitatively defined, the use of this "differential" approach allows us to extract quantitative information from a system where the complete overview of relaxation is lacking.

To ensure good separation of fast heat evolving and heat storing processes, the lifetimes of the fast processes should have an upper limit of ca. $\tau_D/5$, whereas the species storing the energy should have a minimum lifetime of ca. $5\tau_D$. These conditions are fulfilled for PH0, the substrate examined by using this approach.

Singlet oxygen luminescence: Singlet oxygen, $O_2(^1\Delta_g)$, generation efficiencies and kinetics were studied by monitoring its luminescence at 1.27 μm in a time-resolved manner utilizing laser excitation and a germanium diode to provide sensitive detection in the near-IR, as previously described.[23] The 355-nm excitation pulses were provided by the same Nd:YAG laser described above. The laser intensity was heavily attenuated by using a variable-transmission neutral density filter in the excitation path.

Results

The compounds utilized in this study are listed in Chart I. PH1, PH2, and PH7 were synthesized in order to extend the spectral range of the phenothiazine chromophore to 436 nm. All of these sensitizers have been screened in negative resist formulations, and with the exception of PH3 all exhibit sensitivity at either 365 or 436 nm.[24]

Triplet–triplet absorption spectra: Laser excitation of any of the phenothiazines in Chart I in deaerated diglyme solutions led to intense absorption signals; in each case quenching and time-resolved experiments demonstrated that the initial signals are totally or largely due to the triplet state. In the specific case of phenothiazine (PH0), our spectrum agreed well with triplet spectra reported in the literature.[25] Typically the lifetimes were of a few microseconds (vide infra); for example, in the case of PH4 excitation of a ca. 5.5 × 10^{-4} M solution led to a lifetime of ca. 800 ns and a spectrum with λ_{max} 470 nm, quite similar to the value for PH0 (λ_{max} 460 nm); see Figure 1. While most (>90%) of the signals decay in the mi-

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Table I. Spectroscopic and Kinetic Data for the Triplet States of PH0 to PH8 in Diglyme

PHx	$\lambda_{max}{}^{T-T}$, nm	τ_T, μs	$\tau_T{}^{\circ}$,[a] μs	k_{SO},[b] $M^{-1}\,s^{-1}$	$\lambda_{residual}$,[c] nm	$k_q(I)$,[d] $M^{-1}\,s^{-1}$	$E^{\circ\prime}$,[e] V	E_T, eV	$\Delta E(T)$,[f] V
PH0	460	3.5[g]	4.1	2.4×10^8	430, 520	2.6×10^7	0.24	2.60[h,i]	0.96
PH1	560	1.5			470, 530, 600	$\leq 10^6$	0.15	<2.32[j]	
PH2	530	1.5	1.5	$<10^8$	490, 610	$\leq 10^6$	0.18	1.99[i]	0.41
PH3	500	0.85				$\leq 10^6$	0.32	<2.32[j]	
PH4	470	0.8	>10	5×10^8	440, 520	$\leq 10^6$	0.32	2.56[h]	0.86
PH5	475	0.75			450, 560	7.4×10^7	0.19	2.64[h]	1.05
PH6	470	0.6			440, 520	1.6×10^7	0.38	2.70[h]	0.92
PH7	470	0.7			430, 540	$\leq 10^6$	0.34	2.59[h]	0.42
PH8	460	1.0			440, 510	$\leq 10^6$	0.39	2.45[h]	0.66

[a] Triplet lifetime at zero substrate concentration. [b] Estimated error is ±10%. [c] Radical-cation absorption. [d] Estimated error is ±10%. [e] Measured vs Ag/Ag$^+$. [f] Calculated from the equation $\Delta E = E^{\circ\prime}(I^{0/-}) - E^{\circ\prime}(PHx^{+/0}) + E(T)$, where $E^{\circ\prime}(I^{0/-}) = -1.4$ V vs Ag/Ag$^+$. [g] Static cell; all other τ_T values obtained from flow samples. [h] Obtained from low-temperature phosphorescence measurements.[33] [i] Estimated from λ_{max} of heavy-atom solvent (1,2-dibromoethane) induced $S_0 \rightarrow T_1$ absorption band. [j] Value is the upper limit equal to triplet energy of 2,5-dimethylhexadiene that was demonstrated not to quench the PHx triplet state.

crosecond time domain, a small amount of residual absorption can be detected after the triplet decay is complete; even in the absence of I these residual signals appear to be largely due to the corresponding radical cation and may be partially due to self-quenching (vide infra). The triplet–triplet absorption spectra for the nine phenothiazines studied are shown in Figure 1. Only PH1, PH2, and PH3 show ≥40-nm red shifts with respect to PH0; these compounds also exhibit significant red shifts in their ground-state absorption spectra. Spectral data for the triplets have been included in Table I.

The triplet–triplet extinction coefficient for PH0 in acetonitrile, ϵ_T(PH0), was measured by using laser flash photolysis actinometry. The triplet absorbance due to PH0 at its maximum (where no interfering absorption from other transient species is observed) is compared to that of an optically matched solution of an actinometer (A). The corresponding absorbances are related by

$$\epsilon_T(\mathrm{PH0}) = \epsilon_T(\mathrm{A}) \frac{\Phi_{isc}(\mathrm{A})}{\Phi_{isc}(\mathrm{PH0})} \frac{\Delta \mathrm{OD}_T(\mathrm{PH0})}{\Delta \mathrm{OD}_T(\mathrm{A})} \qquad (2)$$

where ΔOD are the observed absorbance changes and Φ_{isc} the intersystem crossing yield. The latter (0.71) and ϵ_T (64 700 $M^{-1}\,cm^{-1}$ at 422 nm) are known for anthracene, the molecule employed as an actinometer, in cyclohexane.[26-29] From data extrapolated to zero laser dose we obtained $\Phi_{isc}\epsilon_T = 22\,200$ $M^{-1}\,cm^{-1}$ for PH0 in acetonitrile at 460 nm. Since $\Phi_{isc} = 0.96$ (vide infra), we obtain $\epsilon_T = 23\,000$ $M^{-1}\,cm^{-1}$. This value is in good agreement with the previously reported values of 23 000[30] and 27 000 $M^{-1}\,cm^{-1}$[25] for *N*-methylphenothiazine in hexane and phenothiazine in methanol, respectively.

Triplet lifetimes and self-quenching: The triplet lifetimes given in Table I (which may incorporate some self-quenching) should simply be taken as the values under which the other experiments performed herein have been largely carried out. Self-quenching frequently plays an important role in determining these lifetimes, and in three selected cases we have examined the self-quenching kinetics (k_{SQ}) in some detail. These experiments were carried out by employing static cells of variable optical path, so that relatively high concentrations could be used while maintaining low absorbances at the laser wavelength. No self-quenching could be detected in the case of PH2 up to 6 mM. In the cases of PH0 and PH4 the decay traces were fitted with first-order kinetics and led to values of k_{decay} that were then plotted against the phenothiazine concentrations. These plots (Figure 2) led to k_{SQ} and τ_0 (the lifetime at zero substrate concentration) according to eq 3, where PHx represents any of the phenothiazines under study.

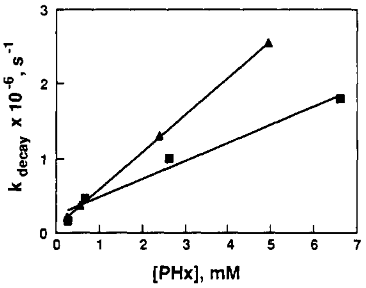

Figure 2. Plot of the observed triplet decay constant as a function of ground-state concentration for PH0 (■) and PH4 (▲) in nitrogen-saturated diglyme.

$$k_{decay} = \tau_0 + k_{SQ}[\mathrm{PH}x] \qquad (3)$$

The values of k_{SQ} obtained for PH0 and PH4 are 2.4×10^8 and 5×10^8 $M^{-1}\,s^{-1}$, respectively. There are also some indications that self-quenching involves a small yield of charge transfer leading to the corresponding radical ions as we observe an increase in the residual absorption following decay of the triplet signal which would signify an increase in nontriplet species; such behavior is not unprecedented.[31,32]

Triplet-state quenching: Quenching of the triplet state can be achieved by a variety of mechanisms; one of these (i.e., self-quenching) has already been described above. Several molecules quench the triplet states of phenothiazines by an energy-transfer mechanism and are very useful for diagnostic purposes. Thus, molecular oxygen quenches the signals of Figure 1 readily. The corresponding rate constants are usually around or slightly over 10^9 $M^{-1}\,s^{-1}$; for example, in the case of PH8 we determined a value of 6×10^9 $M^{-1}\,s^{-1}$. Of course, oxygen is a rather nonspecific quencher, such that quenching by oxygen in itself cannot be employed to characterize unequivocally a triplet state. However, in our case the quenching by oxygen is accompanied by formation of singlet oxygen (vide infra) via energy transfer; combined,

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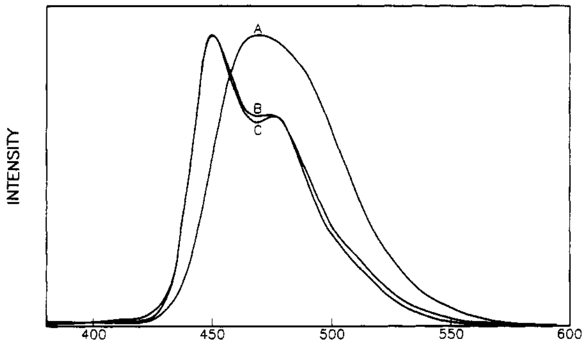

Figure 3. Emission spectra obtained for PH1 in (A) ethanol at room temperature; (B) ethanol glass at 77 K, no delay between excitation and detection; (C) ethanol glass at 77 K, 0.02-ms delay between excitation pulse and detection.

these two results provide conclusive proof for our triplet-state assignments.

Conjugated dienes have been frequently employed as triplet-state quenchers. Their triplet energies are around 57–58 kcal/mol for simple acyclic dienes and around 53 kcal/mol for 1,3-cyclohexadiene. Representative experiments carried out with 2,5-dimethyl-2,4-hexadiene led to a quenching rate constant of 8.4×10^8 M^{-1} s^{-1} for PH0. The value is significantly smaller than rate constants for high-energy triplets (e.g., acetophenone, benzophenone), where energy transfer is ≥10 kcal/mol exothermic. With PH1, PH2, and PH3 no quenching was observed by using either 2,5-dimethyl-2,4-hexadiene or 1,3-cyclohexadiene. For PH1 and PH2 the lack of quenching is unexpected on the basis of triplet energies obtained from previous phosphorescence measurements. With this in mind, combined with our retrospective uneasiness with the almost isoenergetic singlet- and triplet-state energies reported for these compounds,[33] we repeated the measurements and observed that even at 77 K and 0.02-ms detection delay the observed emission spectrum was in fact due to long-lived fluorescence and not phosphorescence, as previously interpreted. This can be demonstrated by the similarity of emission spectra obtained from PH1 at room temperature in ethanol compared to that obtained at 77 K in an ethanol glass as a function of delay between excitation pulse and detection of emission, shown in Figure 3. No actual phosphorescence emission was observed for these compounds. The lack of significant triplet energy transfer quenching by 1,3-cyclohexadiene infers an upper limit of 53 kcal mol^{-1} for the triplet energies of PH1 and PH2, as well as for PH3.

Triplet quenching by I, which is believed to involve charge transfer, occurs efficiently (i.e., with $k_q > 10^6$ M^{-1} s^{-1}) for only three of the phenothiazines in Table I, where the corresponding values have been included. Quenching of halogenated compounds is not unique to I; 1,2-dibromomethane (II) is also a good quencher although much less efficient than I. For PH0 the rate constants for quenching by I and II in diglyme and acetonitrile are 2.6×10^7 and 4×10^6 M^{-1} s^{-1}, respectively. Figure 4 shows representative plots for the quenching of PH0 and PH5 by I. In all the cases examined electron-transfer quenching by I is at least 1 eV exothermic, as based on redox potentials determined in dry acetonitrile. In these experiments the residual absorption following triplet decay increases with increasing I concentration, consistent with an increase in the production of radical ions; however, the initial triplet absorption (i.e., at the end of the laser pulse) decreases, showing that singlet quenching is also taking place. Thus, interpretation of the data in terms of a triplet electron-transfer mechanism is not straightforward. In some cases, such as PH5, comparison of transient spectra in the presence of I under nitrogen or air saturation shows a decrease of the radical cation (vide infra) absorption in the presence of air. This suggests that at least a fraction of the radical cations are produced via triplet quenching.

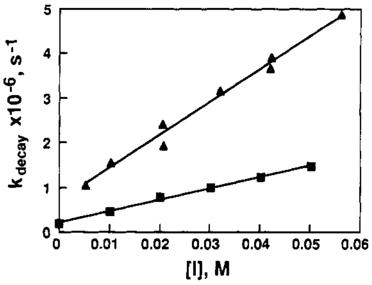

Figure 4. Plot of the observed triplet decay constant as a function of the concentration of I for PH0 (■) and PH5 (▲) in nitrogen-saturated diglyme.

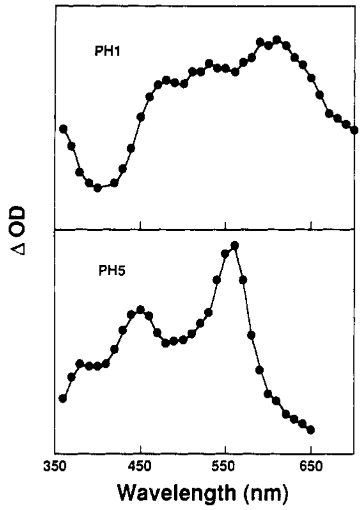

Figure 5. Absorption spectra of radical cations of PH1 (upper) and PH5 (lower) recorded following quenching of triplet state by I in air-saturated diglyme.

Intersystem crossing yields: Φ_{isc} values were measured by using the novel differential LIOAC approach, as described. Preliminary experiments on PH0 in two different solvents illustrated that intersystem crossing is a very efficient process. In acetonitrile, from eq 1 we calculate the product of Φ_{isc} and E_T to be $(0.937 - 0.243) \times 80.7 = 58.9$ kcal mol^{-1}, and as E_T is known from phosphorescence measurements to be 61 kcal mol^{-1} a value of 0.96 for Φ_{isc} is obtained. In diglyme, α(ii) and α(i) values of 0.981 and 0.395, respectively, were measured resulting in a Φ_{isc} value of 0.77 in this solvent.

Radical-cation characterization and spectroscopy: Radical cations usually do not react with oxygen in the time scale (~10^{-6} s) involved in these experiments. On the other hand, other intermediates, such as triplets (vide supra), singlets, and radical anions are usually scavenged/quenched with rate constants in excess of 10^9 M^{-1} s^{-1}. Further, the radical and radical anion from I would not be anticipated to have significant absorptions that could interfere with phenothiazine-derived transients. Thus, examination of transient spectra in air-saturated solutions leads to relatively clean spectra of the phenothiazine radical cations; some representative spectra are

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[33] Calabrese, G. S.; Lamola, A. A.; Sinta, R.; Thackeray, J. W.; Berry, A. K. *Proc. Int. Symp. Polym. Microelectron. (Tokyo)* **1989**, 70.

Table II. Singlet Oxygen Generating Efficiencies, Rate Constants of Singlet Oxygen Quenching, and Ground-State Extinction Coefficients for PH0 to PH8 in CH_3CN

PHx	Φ_Δ	kq for $O_2(^1\Delta_g)$,[a] $M^{-1}\ s^{-1}$	ϵ_{336}, $M^{-1}\ cm^{-1}$
PH0	0.20	5.6×10^7	3100
PH1	~0.2	4.2×10^8[b]	3600
PH2	~0.17	2.3×10^8[b]	3500
PH3	~0.46	not measd	3200
PH4	*c*	not measd	3600
PH5	0.21	2.0×10^8[b]	3600
PH6	0.19	8.2×10^6	1800
PH7	0.19	2.9×10^7	4900
PH8	0.18	1.2×10^7	3200

[a] Estimated error is ±10%. [b] Obtained by using acetonitrile-d_3. [c] $O_2(^1\Delta_g)$ luminescence was detected, but sample instability ruled out quantitative measurements.

shown in Figure 5, and λ_{max} values for radical cation absorptions are listed in Table I. Signals are moderately intense in all cases with PH5 exhibiting a significantly larger signal than the others. In the case of PH2 we have established that in the presence of I the radical cation is formed exclusively from the singlet manifold.

Singlet oxygen studies: An important factor in photoresist applications is their "shelf life" and general photostability. The phenothiazines studied here are rather unstable toward irradiation once in solution. In particular, it is of interest to test the photoreactivity of these compounds in the presence of oxygen. To this end we have examined the efficiencies with which the phenothiazines of Chart I generate singlet oxygen, as well as the kinetics with which these molecules scavenge singlet oxygen. Both these studies involved the detection of singlet oxygen phosphorescence at 1.27 μm by using a germanium photodiode for detection (see Experimental Section). The quantum yields (Φ_Δ) of $O_2(^1\Delta_g)$ production were measured by comparing signal intensities to that of a standard substrate in the same solvent whose Φ_Δ value is known. The standard employed in these experiments was phenazine, for which $\Phi_\Delta = 0.83$ in acetonitrile (the solvent used in these experiments). Φ_Δ values are given in Table II and are consistently around 0.2 with the exception of PH3, for which we determined $\Phi_\Delta = 0.46$. The latter Φ_Δ value serves as a lower limit for the intersystem crossing yield, Φ_{isc}, of PH3 (which, due to lack of quenching by 2,5-dimethylhexadiene, could not be measured by LIOAC) given that singlet oxygen formation is mediated solely through the triplet state, as singlet sensitization is not energetically feasible for these compounds. Interestingly, PH3 is a rather poor sensitizer for photoresist applications, which may suggest that the singlet state can play an important role in photoacid generation.

Rates of reaction of singlet oxygen with ground-state phenothiazines were obtained by production of $O_2(^1\Delta_g)$ either through the phenothiazine itself or by an added singlet oxygen sensitizer and investigating the change in phosphorescence lifetime in the presence of varying concentrations of the phenothiazines (concentrations were calculated by using the extinction coefficients given in Table II). This allows the evaluation of the quenching constants, $k_q(^1O_2)$, as shown in Figure 6. The values obtained have been included in Table II. Clearly, these high rate constants, combined with the modest but significant yields for singlet oxygen formation observed could partly explain the instability of these compounds.

Fluorescence studies: Steady-state fluorescence studies reveal similar spectra for most of the phenothiazines, with λ_{max} in the neighborhood of 450 nm (see Table III). The only exceptions are again PH1, PH2, and PH3, which are significantly red shifted; clearly, the presence of these conjugated chromophores changes significantly the spectroscopic properties of the sensitizers. Stern–Volmer studies for the quenching by I in aerated solutions were carried out by monitoring the emission intensity for various concentrations of I following excitation at 337 nm. Figure 7 shows two representative Stern–Volmer plots and in the insert the emission spectra for PH6. The Stern–Volmer data have been summarized in Table III.

Fluorescence lifetimes were determined by single-photon counting and were generally rather difficult to measure in our instrument as a result of the short lifetimes involved. Some of these measurements were further complicated by the weak but long-lived emissions which we presume are due to trace impurities in the samples; attempts to completely eliminate these were unsuccessful, probably as a result of the intrinsic instability of some of these substrates

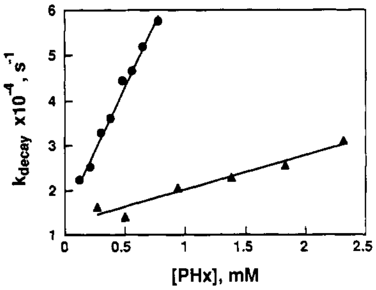

Figure 6. Plot of the observed rate constant for decay of singlet oxygen as a function of concentration of PH0 (●) and PH6 (▲) in oxygen-saturated acetonitrile.

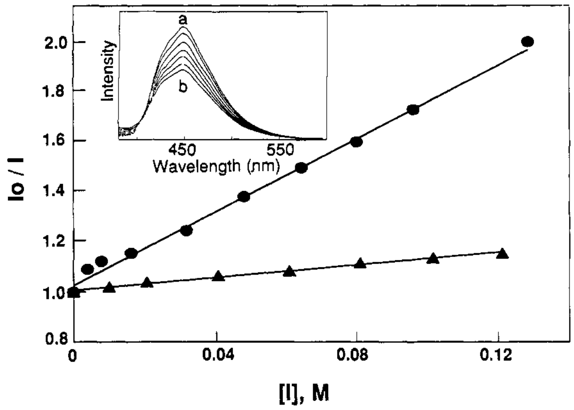

Figure 7. Stern–Volmer plot for quenching of fluorescence emission from PH5 (●) and PH8 (▲) by I in air-saturated diglyme (inset, decrease in emission from PH6 as the concentration of I is increased from 0 to 0.12 M).

Table III. Singlet-State Quenching Data for PH0 to PH8 in Diglyme

PHx	τ_s,[a] ns	λ_{max},[h] nm	$k_q\tau_s$,[c] M^{-1}	k_q(fluorescence),[d] $M^{-1}\ s^{-1}$	E_s, eV	ΔE(S),[e] V
PH0	≤1	442	7.2	$\geq 7.2 \times 10^9$	3.09	1.45
PH1	22	500	8.9	4.0×10^8	2.76	1.21
PH2	20	505	5.3	2.6×10^8	2.75	1.17
PH3	11	532	2.8	2.5×10^8	2.65	0.93
PH4	≤1	450	1.4	$\geq 1.4 \times 10^9$	2.96	1.22
PH5	≤1	446	7.2	$\geq 7.2 \times 10^9$	3.06	1.47
PH6	1.6	447	6.3	3.9×10^9	3.19	1.41
PH7	≤1	443	1.1	$\geq 1.1 \times 10^9$	3.06	1.34
PH8	2.5	471	1.3	5.2×10^8	2.96	1.17

[a] Fluorescence lifetimes under air. [b] Fluorescence. [c] Estimated error is ±10%. [d] Estimated error is ±15%. [e] Calculated from the equation $\Delta E(S) = E^{\circ\prime}(I^{0/-}) - E^{\circ\prime}(PHx^{+/0}) + E(S)$, where $E^{\circ\prime}(I^{0/-}) = -1.4$ V vs Ag/Ag^+.

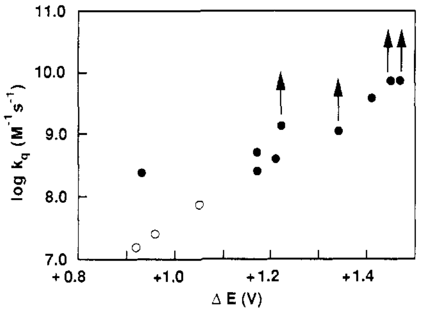

Figure 8. Plot of the observed rate constant for electron transfer quenching of phenothiazine singlet (●) and triplet states (○) as a function of ΔE; taken from the last columns of Tables I and III. Arrows indicate direction of possible movement of points which are minimum values.

(vide supra). Only in the cases of PH1, PH2, and PH3 were the measurements straightforward. Combination of the time-resolved and Stern–Volmer data allows the estimation of singlet quenching rate constants; these, along with the corresponding redox properties, have been included in Table III.

Interestingly, the singlet quenching data indicate that under typical conditions of photoresist applications most of the photosensitizing role of the phenothiazines may involve singlet processes. Indeed, the high efficiency of radical-cation formation from the singlet state (vide supra) supports this interpretation.

Conclusion

Clearly the mechanism for phenothiazine quenching by I involves electron transfer, which ultimately leads to photoacid generation. Interestingly, the rates of excited-state quenching for those molecules where the measurements were feasible correlate well in a single plot for both singlets and triplets (Figure 8). The points for those systems where we were able to determine only a lower limit to k_q as a result of the short singlet lifetime have been identified with an arrow and in general fit rather well; in the cases of PH0 and PH5 the values are sufficiently close to the diffusion limit that one should not anticipate much variation from the position displayed in Figure 8. The origin of the deviation for PH3 is unclear, although it is possible that the ketone substituent introduces enough of a perturbation in the chromophore to alter significantly its behavior.

The photochemistry of seven of the nine molecules examined in this work had not been reported before. Clearly, the basic behavior remains much the same throughout the group. Increased delocalization (as in PH1 and PH2), which makes these molecules better candidates for photoresist applications employing the mercury lamp g line (436 nm), also reduces the electron-donor ability of the triplet state toward molecules such as I. It is very likely that the ability of molecules such as PH1 and PH2 to act as photosensitizers is related more to their singlet than to their triplet state. Fluorescence quenching studies show that while these molecules are less reactive than PH0, the rate constants (see Table III) remain high enough for them to be useful. All the phenothiazine triplets are modest singlet oxygen sensitizers.

The overall complexities in these systems have led us to propose a new "differential" approach for the use of optoacoustic spectroscopy for the determination of intersystem crossing yields. This method proved readily applicable to PH0.

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Registry No. I, 52434-90-9; PH0, 92-84-2; PH1, 225-83-2; PH2, 226-06-2; PH3, 6631-94-3; PH4, 92-39-7; PH5, 1771-18-2; PH6, 1207-72-3; PH7, 258-08-2; PH8, 92-30-8; O_2, 7782-44-7.

X-ray Photoelectron Spectroscopic Depth Profiling of an Atomic Oxygen Resistant Poly(carborane–siloxane) Coating

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A novel, self-healing atomic oxygen resistant coating based on poly(carborane–siloxane) has been developed. Scanning electron microscopy studies of coated specimens after exposure to an atomic oxygen environment showed a distinct glassy layer on the surface. XPS depth profiles from such layers were processed by nonlinear curve-fitting methods to yield smooth, continuous atomic concentration curves. A depletion in the boron content was observed near the surface of the glassy layer. The glassy layer has a silica composition at the surface and approaches the borosilicate composition at deeper levels. High oxygen levels prevail beneath the glassy layer, indicating that the original polymer was oxygenated by atomic oxygen. The nonlinear smoothing of the depth profile curves is a powerful method to determine atomic ratios from the inherently noisy data.

Introduction

Atomic oxygen degradation of organic materials has been extensively studied in recent years.[1-4] According to these studies, most polymers and polymer matrix composites are not adequate for low earth orbit (LEO) space structures

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[2] Banks, B. A.; Rutledge, S. K. Low Earth Orbital Atomic Oxygen Simulation for Materials Durability Evaluation. In *The Fourth Int. Symp. on Spacecraft in Space Environment*; Tolouse, France, Sep 1988; p 121.

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