Mechanistic Studies of Photoacid Generation from Substituted 4,6-Bis(trichloromethyl)-1,3,5-triazines

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The photochemistry and photophysics of 2-methyl- (**1**), 2-(2′-furylethylidene)- (**2**), and 2-[(4′-methoxy)styryl]-4,6-bis(trichloromethyl)-1,3,5-triazine (**3**), three compounds that find application as photoacid generators in photoresist formulations, have been investigated under conditions of direct excitation and using various phenothiazine derivatives as photosensitizers. C−Cl bond cleavage is confirmed by laser flash photolysis as the primary photochemical step in the direct photolysis of these compounds; the chlorine atoms formed in this reaction can be detected by complexation with chloride anions or benzene. In the case of **1**, this photodissociation occurs with a lifetime of <20 ns. The quantum yield of bond breaking for **1** after direct excitation as determined by laser flash photolysis and steady-state irradiations was found to be 30−40 times greater than for **2** and **3**. The mechanism under sensitized conditions involves electron transfer from the excited phenothiazines to the triazines as the primary photochemical step; the rate constants for excited-state quenching exceed 10^9 M^{-1} s^{-1} for the T_1 state and 10^{10} M^{-1} s^{-1} for the S_1 state. The rate constants correlate with the free energy for electron transfer estimated from the excited-state energies and the oxidation potential of the sensitizers.

Introduction

Modern microlithographic techniques employed for image transfer in semiconductor applications rely heavily on photoinduced generation of acid. In the case of *positive resists*, generation of acid assists in the solubilization of a thin polymer film in the exposed areas. In the case of *negative resists*, exposure leads to a decrease in film solubility, usually achieved through cross-linking of the polymer.[1−3] Phenolic polymers (such as novolac) are widely employed in the microelectronics industry. A wide range of acids can be generated by a variety of photoacid generators (PAGs), including carboxylic acids, sulfonic acids, hydrogen bromide, and hydrogen chloride.

(Trichloromethyl)-1,3,5-triazines are an important class of photoinitiators and PAGs for photoacid generation of HCl, and many substituted triazines have been reported in the patent literature.[4] These are usually 4,6-bis(trichloromethyl)-1,3,5-triazines substituted in the 2 position with a suitable chromophore. This chromophore modifies the absorption characteristics of the unsubstituted compound in order to extend the wavelength range of the response. A second way of extending the spectral sensitivity of the PAGs is photosensitization of the triazine using an appropriate sensitizer that absorbs in the spectral region of interest.

Surprisingly, no detailed studies of (trichloromethyl)-1,3,5-triazine photochemistry upon direct excitation or under sensitized conditions have been reported so far. On the basis of product studies following photolysis of various 2-substituted 4,6-bis(trichloromethyl)-1,3,5-triazines in solution, Buhr et al.[5] have proposed that the mechanism of HCl generation from these compounds involves homolysis of a carbon−chlorine bond. In another study, Kawamura et al.[6] have carried out experiments employing merocyanine dyes as photosensitizers for 2,4-bis(trichloromethyl)-1,3,5-triazines. They observed quenching of the dye fluorescence by the triazines and proposed electron transfer from the excited dye to the triazine to be responsible for this observation. Since both studies employed rather indirect techniques, we tried to verify the proposed mechanisms by direct observation of the reaction intermediates and to gain more insight into mechanistic details of this type of reaction, e.g., measuring absolute rate constants of electron transfer and bond cleavage.

In the first part of our studies, we explored the utility of three 4,6-bis(trichloromethyl)-1,3,5-triazines (see Chart 1) as PAGs for HCl generation upon *direct excitation*. The methyl-substituted derivative was incorporated into our study in order to investigate the effect that the

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Chart 1

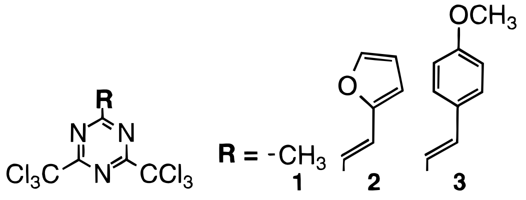
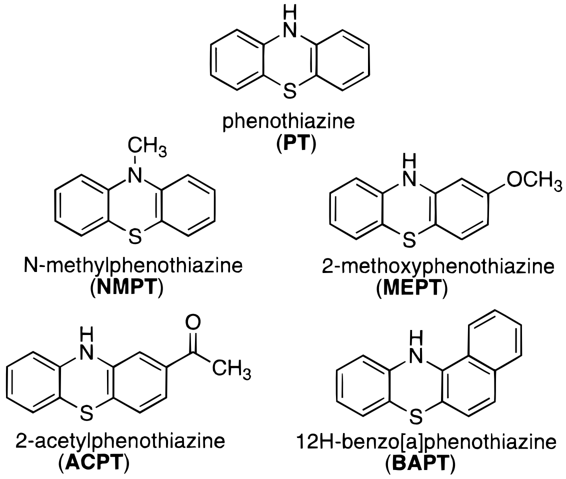


Chart 2



introduction of the unsaturated side chain has on the efficiency of photoacid generation. Compounds **2** and **3** are particularly interesting because these PAGs are used in a variety of imaging applications.

In the second part, we investigated the use of phenothiazines as *photosensitizers* for these triazines. These compounds have proven to be effective in earlier studies on hydrogen bromide generation.[7,8] By investigating a series of compounds with different oxidation potentials and excitation energies we were able to study the effect that variation of these parameters has on the feasibility of electron transfer.

Our studies are based on a combination of laser flash photolysis work, picosecond and steady-state fluorescence spectroscopy, and analytical evaluation of acid formation.

Experimental Section

Materials. The triazines **1**−**3** used are shown in Chart 1. Compound **1** was purchased from Panchim and purified by recrystallization from methanol (2×) and subsequent sublimation. The triazines **2** and **3** were obtained from Panchim, and recrystallized two times from ethanol.

Phenothiazine (PT) and ACPT (Chart 2) were obtained from Aldrich. PT was recrystallized from toluene in the presence of charcoal and sublimed. ACPT was recrystallized from toluene, sublimed, and then recrystallized from ethanol again. MEPT and NMPT were purchased from TCI and Kodak, respectively, and purified by sublimation. BAPT was prepared by the method of Purnendu et al.,[9] and the crude product sublimed and finally recrystallized from ethanol. The purity of the phenothiazines was checked using fluorescence excitation spectroscopy and time-resolved fluorescence; all showed monoexponential fluorescence decays.

Tetramethylammonium chloride (TMAC), benzophenone, and valerophenone were obtained from Aldrich. TMAC was recrystallized twice from ethanol prior to use. Acetonitrile, diglyme, and benzene were from BDH and used as received.

General Techniques. Absorption spectra were recorded using a Varian CARY 1E spectrophotometer. Fluorescence spectroscopy was carried out using a Perkin-Elmer LS-50 luminescence spectrometer. Suprasil quartz cells with a 10 mm optical path were employed in all these experiments. Phosphorescence experiments were performed at 77 K (EtOH/MeOH 4:1 glass) using a quartz dewar and 5 mm NMR sample tubes.

Steady-state irradiations were performed at 30−35 °C in a photoreactor equipped with RPR-300 nm lamps from the Southern New England Ultraviolet Co. The quartz cells used for these experiments were rotated using a "merry-go-round" apparatus to ensure that all samples received the same irradiation dose.

Laser Flash Photolysis. For the nanosecond laser flash photolysis work, a Lumonics EX-510 excimer laser (Xe/HCL, 308 nm, ~6 ns pulse width, 50−80 mJ/pulse) was used for excitation for most of the experiments. In the experiments with biphenyl, a Molectron UV-24 nitrogen laser (337.1 nm, ~8 ns pulse width, 6 mJ/pulse) was used for excitation. The third harmonic of a Surelite Nd:YAG laser (355 nm, ~6 ns pulse width, ≤20 mJ/pulse) was used when **1** was employed as a quencher for the phenothiazine derivatives. The system is controlled by a PowerPC Macintosh computer running LabVIEW 3.1.1 software (National Instruments). A Tektronix 2440 digital oscilloscope is used to capture and digitize the signal from the photomultiplier tube. Detailed descriptions of similar laser systems have been provided elsewhere.[10,11]

In all experiments a flow system (a 7 × 7 mm Suprasil quartz flow cell that is connected to a reservoir with Teflon tubing) was used. The flow technique was the method of choice due to the photolability of the investigated PAGs and phenothiazines. Unless otherwise stated, all samples were deaerated by bubbling with oxygen-free nitrogen for 15 min.

Time-Resolved Fluorescence. For the picosecond time-resolved fluorescence experiments, the third harmonic (355 nm) of a Continuum PY61-10 laser (~0.5 mJ/pulse, 30 ps pulse width) was used for excitation. A Hamamatsu C4334 streak camera and software is utilized for detection and data acquisition. Due to the relatively low laser power and the small number of shots used in these experiments, deterioration of the samples was negligible, and all experiments could be carried out in static 7 × 7 mm Suprasil quartz cells.

Determination of Quantum Yields of Acid Production. In these experiments, 3 mL of a 0.05 M solution of **1**−**3** in diglyme in a quartz cell was deoxygenated by purging with oxygen-free nitrogen for 15 min, sealed, and irradiated in the photoreactor at 300 nm. The HCl concentration was determined by acid−base titration in methanol using phenolphthalein as indicator and a 0.01 M solution of NaOH in methanol as titrant. The Norrish II reaction of valerophenone in benzene ($\Phi = 0.30$)[12] was employed as actinometer.

Results and Discussion

Direct Excitation. *Photophysics.* The absorption spectra of **1**−**3** are shown in Figure 1. The spectrum of **1** is the typical spectrum of the triazine chromophore, and we assume that the lowest excited singlet state of **1** can be described by a n,π^* excited-state configuration, as is the case for the parent molecule 1,3,5-triazine. For this molecule, the weak band due to the n,π^*-transition is masked by the more intense π,π^* transition. In these

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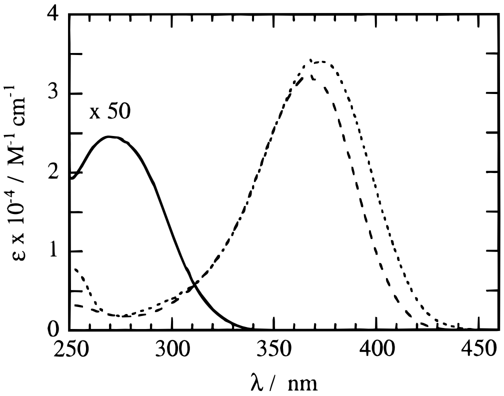


Figure 1. Absorption spectra of **1**−**3** in acetonitrile at room temperature; **1** (—), **2** (− − −), and **3** (- - -).

Table 1. Extinction Coefficients (ϵ) of the Long-Wavelength Absorption Band, Singlet Energies (E_S), and Quantum Yields for Chlorine Atom ($\Phi_{Cl^\bullet}$) and HCl (Φ_{HCl}) Photogeneration upon Direct Excitation of Triazines 1−3 at Room Temperature

triazine	ϵ (λ_{max})^a (M^{-1} cm^{-1})	E_S^{a} (kcal mol^{-1})	$\Phi_{Cl^\bullet}$^{a}	Φ_{HCl}^{b}
1	490 (270 nm)	87	0.40 (N_2)/0.40 (O_2)	0.45
2	32 400 (368 nm)	73^c		0.010
3	34 000 (370 nm)	72^c		0.012

[a] In acetonitrile. [b] In deaerated diglyme. [c] Estimated from the point of inflection of the long-wavelength absorption band.

cases, the position of the n,π* band can be roughly estimated from the wavelength where $\epsilon = 20$.[13] Applying this method to the electronic spectrum of **1** yields E_S = 87 kcal/mol, in good agreement with the values reported for 1,3,5-triazine before (90[13] and 88.5 kcal/mol[14]). The observed slight decrease in S_1 energy of **1** relative to the parent compound is probably due to the substitution in **1**.

The unsaturated side chain at the 2-position causes a significant red-shift and a drastic increase in extinction coefficient of the long-wavelength band in the absorption spectra of **2** and **3**. Certainly, the lowest excited singlet state of **2** and **3** cannot be described by a locally excited configuration of the triazine moiety any more, and assigning the S_1 state to an electronic configuration is not straightforward. The available spectroscopic data for **1**−**3** are listed in Table 1.

All three triazines were found to be nonfluorescent. In the case of **1** this is not surprising considering the electronic nature of the S_1 state (n,π*) and the fact that the radiative deactivation of the S_1 state has to compete with photodissociation (Scheme 1). This is believed to be a very fast process for **1** (vide infra). In the case of **2** and **3** it is not clear which process is responsible for the very low fluorescence quantum yield, but from the lack of phosphorescence, it is inferred that this is not due to efficient intersystem crossing (unless the triplet state of **2** and **3** is depopulated by a relatively fast radiationless process that makes the radiative deactivation of the T_1 state of these molecules very inefficient).

Since the triplet state of **1**−**3** cannot be observed directly with our methods, the triplet energy of **1** was estimated from the triplet energies that are available for 1,3,5-triazine in the literature. Hochstrasser and Zewail[15] report 82.6 kcal/mol, whereas Paris et al.[16] estimate the T_1 energy of 1,3,5-triazine to be 71.5 kcal/mol. Considering the reported S_1 energy of 88−90 kcal/mol and the electronic configuration of both the S_1 and T_1 state (n,π*), the singlet−triplet energy gap of ~6 kcal/mol as calculated from Hochstrasser's value seems to be more reasonable than the ~16 kcal/mol based on the triplet energy reported by Paris et al. Taking into account the effect of substitution, the triplet energy of **1** is estimated to be about 80 kcal/mol. Due to the lack of a model compound for **2** and **3**, we were unable to estimate the triplet energy of these molecules in a similar manner.

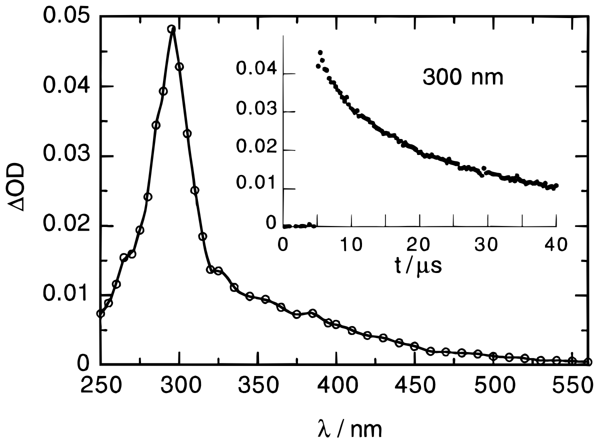
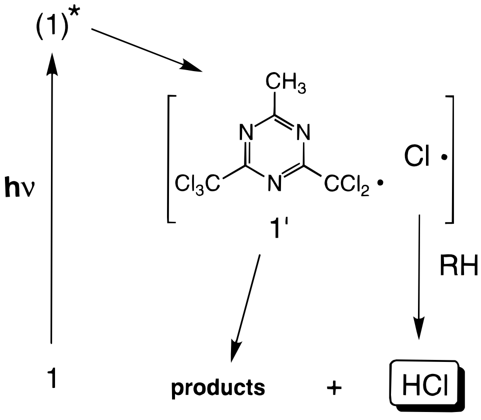


Figure 2. Transient spectrum recorded following 308-nm laser excitation of **1** in deaerated acetonitrile. Inset: Decay of the signal at 300 nm (attributed to **1′**) under the same conditions.

Scheme 1



Laser Flash Photolysis. The transient spectrum recorded after 308 nm laser excitation of **1** in deaerated acetonitrile is shown in Figure 2. The decay of this transient was monitored at 300 nm (see inset in Figure 2) and follows clean second-order kinetics ($2k_t/\epsilon l = 2.8 \times 10^6$ s^{-1}). The intensity and shape of the spectrum are not affected by oxygen, whereas the lifetime of the transient in an oxygen-purged solution is significantly shortened, now following a pseudo-first-order kinetics ($k = 1.8 \times 10^6$ s^{-1}). On the basis of these observations, we conclude that homolysis of the C−Cl bonds is the primary photochemical step and assign the spectrum

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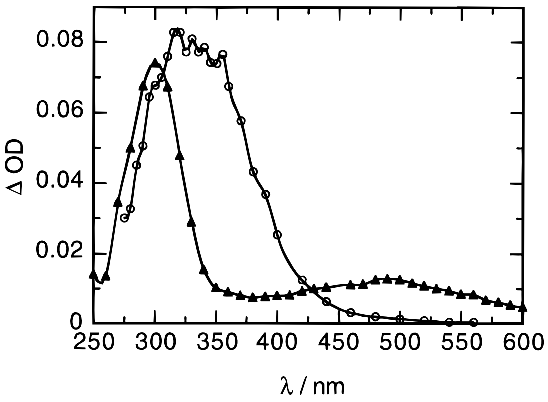


Figure 3. Same as Figure 2 but in the presence of 5 mM TMAC (○) and benzene (▲).

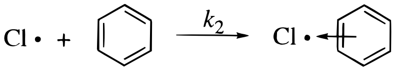
in Figure 2 to the organic radical **1**′ that is formed by breaking one of the carbon−chlorine bonds in **1**; this is summarized in Scheme 1.

To confirm that the primary photochemical step is the homolysis of a carbon−chlorine bond, we tried to detect the chlorine atoms that should occur concurrently with the formation of **1**′. Since chlorine atoms are not detectable directly with our system, we used tetramethylammonium chloride (TMAC) to make them "visible". Chloride anions form a well-characterized complex with chlorine atoms:[17]

$$\mathrm{Cl}^{\bullet} + \mathrm{Cl}^{-} \xrightarrow{k_1} \mathrm{Cl_2}^{\bullet -} \tag{1}$$

The rate constant for reaction **1** in acetonitrile is 1.3 × 10^{10} M^{-1} s^{-1}, and the complex is readily detectable between 300 and 400 nm. As shown in Figure 3, 308 nm laser excitation of **1** in deaerated acetonitrile in the presence of 5 mM TMAC leads to a new band at 320 nm due to $Cl_2^{\bullet -}$, thereby establishing the formation of chlorine atoms upon photolysis of **1**. The chlorine atom formed then abstracts a hydrogen atom from either the solvent or the PAG; the latter pathway is probably relevant only in the case of **1** due to the relatively high concentration typically used (∼3 × 10^{-3} M), compared to ∼2 × 10^{-5} M for **2** and **3**.

A second way of detecting chlorine atoms is monitoring the CT complex between benzene and $Cl^{\bullet}$:[18]



(2)

This complex ($k_2 = 6 \times 10^9$ M^{-1} s^{-1})[19] exhibits two easily detectable bands at 490 and 310 nm. The spectrum of **1** in acetonitrile following laser excitation at 308 nm and in the presence of 20 mM benzene (Figure 3) is in good agreement with the spectra reported for the complex in the literature,[18,19] except that the UV band is too intense compared to the band at 490 nm, which we attribute to the contribution of **1**′ ($\lambda_{max} = 295$ nm) to the signal at 300 nm.

At high scavenger concentrations (∼20 mM) the formation of the both the $Cl_2^{\bullet -}$ and the $Cl^{\bullet}$/benzene complex appears to be instantaneous within the time resolution of our system, i.e., the photodissociation occurs with a lifetime of <20 ns at room temperature.

Since the triplet state of **1** could not be observed directly, we tried to determine its triplet lifetime by an indirect approach. We employed biphenyl as a triplet quencher and excited **1** at 337 nm, where biphenyl is transparent. Under these conditions, **1** is excited exclusively, and any formation of triplet biphenyl must be due to energy transfer from triplet-**1** to biphenyl; i.e.

$$\mathbf{1} \xrightarrow{h\nu} {}^{1}(\mathbf{1})^{*} \xrightarrow{\text{isc}} {}^{3}(\mathbf{1})^{*} \tag{3}$$

$${}^{3}(\mathbf{1})^{*} + \mathrm{Bip} \xrightarrow{k_q} {}^{3}\mathrm{Bip}^{*} + \mathbf{1} \tag{4}$$

Biphenyl was chosen because of its combination of a relatively high-lying S_1 state ($E_S = 96$ kcal/mol) which allows selective excitation of **1** at 337 nm (ϵ_{337}[bip] ≤ 0.02 M^{-1} cm^{-1}) and a low-energy triplet state (E_T[bip] = 65.8 kcal/mol,[20] E_T [**1**] ≈ 80 kcal/mol). Thus, triplet−triplet energy transfer would be exothermic by ∼14 kcal/mol. Furthermore, the spectrum of the biphenyl triplet has a sharp, very intense maximum at ∼360 nm,[21] and finally, biphenyl exhibits an excellent solubility in acetonitrile. The transient absorbance (ΔOD) of the biphenyl triplet at 360 nm is related to the quencher concentration [Bip], the triplet lifetime τ_T of **1** and the rate constant k_q as follows:[22]

$$\frac{1}{\mathrm{OD}_{360}} = a + \frac{a}{k_q \tau_T [\mathrm{Bip}]} \tag{5}$$

where a is a constant including experimental parameters and the quantum yield of intersystem crossing of **1**. However, we were unable to detect any signal due to sensitized formation of triplet biphenyl at quencher concentrations up to 0.8 M. This means that the triplet state of **1** is either not populated significantly or its lifetime is too short (τ_T < 0.1 ns) to enable sensitization of the biphenyl triplet. The fact that we were unable to detect a phosphorescence at 77 K for **1** suggests a very low triplet yield, unless a very efficient $T_1 \rightarrow S_0$ intersystem crossing deactivates the triplet state of **1** even at 77 K. A deactivation of this type has been postulated in order to explain the lack of phosphorescence of pyridine.[23]

The transient absorption spectra measured after 308 nm laser excitation of **3** in deaerated acetonitrile is shown in Figure 4, it shows close resemblance with the spectrum of **2** (not shown) under the same conditions, illustrating the structural similarity between these two molecules. The dominant feature in both spectra is the extensive ground-state bleaching. Furthermore, both spectra exhibit a fairly weak absorption between 450 and 650 nm. An additional signal at 410 nm observed for **2** is mainly due to a stable photoproduct since it does not decay even in the millisecond time domain.

Although the absorption band due to the $Cl_2^{\bullet -}$ complex cannot be detected directly in the transient spectrum of **3** recorded after laser excitation in the presence of 5 mM TMAC (Figure 4), the changes in the region

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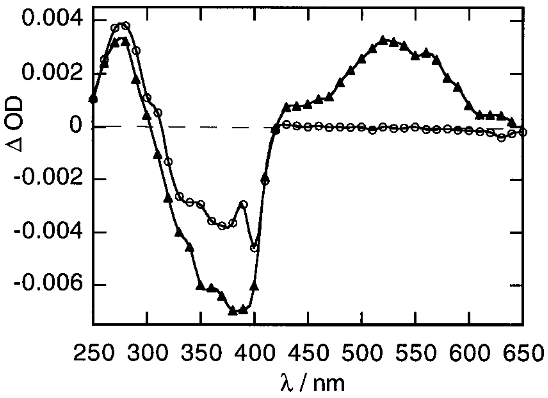

Figure 4. Transient spectrum recorded following 308-nm laser excitation of **3** in deaerated acetonitrile without (▲) and with (○) 20 m M TMAC.

between 300 and 400 nm relative to the spectrum without TMAC clearly indicate its formation. Analogous observations were made for **2**, and thus we conclude that the same mechanism already outlined in Scheme 1 for PAG **1** is also valid for the triazines **2** and **3**. The finding that the photobleaching signal still dominates the overall signal in that region shows that **3** has a lower quantum yield of chlorine atom formation than **1**. Interestingly, the transient absorption centered at 550 nm is completely quenched by added chloride (see Figure 4). This indicates that this band is probably due to a complex formed between the chlorine atoms and **3**. If TMAC is added to the sample, the chloride and **3** compete for the chlorine atoms formed, and due to the approximately 200 times higher concentration of TMAC most of the Cl$^{\bullet}$ is now scavenged by the chloride. Assuming a rate constant for complex formation between Cl$^{\bullet}$ and **3** of $\sim 1 \times 10^{10}$ M^{-1} s^{-1} and taking into account that the concentration of **3** was only $\sim 1 \times 10^{-4}$ M, we thought that we may be able to time resolve the complex formation. However, we failed to observe a growth at 520 nm. Analogous observations were made for **2** in the presence of TMAC. Since the growth kinetics would reflect the lifetime of the highly reactive chlorine atom,[19] it is very likely that it is very short lived, even in a moderately inert solvent such as acetonitrile. Thus, the growth of the complex may be quite fast, reflecting other reaction paths for the chlorine atom and a low yield of complexation.

In a second attempt to detect chlorine atoms formed upon irradiation of **2** and **3** we used benzene as a scavenger since the long-wavelength band of the benzene/Cl$^{\bullet}$ complex can be monitored in a region where no photobleaching occurs. Contrary to the experiment employing chloride (not shown for **2**), there are no significant changes in the spectrum compared to the sample without scavenger; an analogous observation was made for **3**. This lack of quenching of the absorption attributed to the complex between Cl$^{\bullet}$ and **2** and **3**, respectively, is surprising since both the rate constants for complexation and the concentration of scavenger used were almost the same for Cl^{-} and benzene.

No signal due to the radicals **2′** or **3′** could be detected; this is not surprising considering the low quantum yield of chlorine atom formation from **2** and **3** (vide infra). Given the lack of information on the triplet energies of **2** and **3**, no quenching studies were carried out with these compounds.

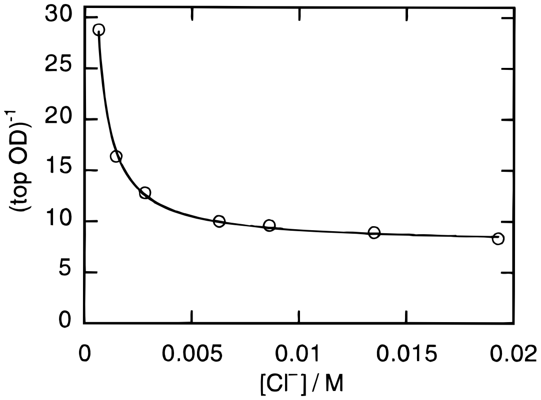

Figure 5. (Top OD)$^{-1}$ of the Cl$_2^{\bullet-}$ complex in deoxygenized acetonitrile as a function of chloride concentration. The line represents the best fit of eq 7 to the experimental data.

Quantum Yields. Since the quantum yield of chlorine atom formation for **1**–**3** should be identical with the quantum yield of Cl$_2^{\bullet-}$ formation at chloride concentrations high enough to ensure quantitative trapping of Cl$^{\bullet}$, the quantum yield of the photodissociation can be quantified by monitoring the signal of this complex (ϵ_{355} = 7100 M^{-1} cm^{-1})[17] and using a suitable actinometer. We employed benzophenone in benzene as actinometer, since its triplet state has a very well characterized,[24] intense signal ($\lambda_{\max}$ = 525 nm, ϵ_{525} = 7800 M^{-1} cm^{-1}) and a quantum yield of triplet formation of 1.0. In these experiments, we measured the change in transient absorption of the Cl$_2^{\bullet-}$ complex and the actinometer as a function of laser dose. The optical densities at the excitation wavelength (308 nm) of **1** and the actinometer had been carefully matched; the values obtained this way are listed in Table 1.

This method requires that the trapping of chlorine atoms by chloride be quantitative. Therefore, we made an attempt to determine the chloride concentration that would ensure quantitative trapping of the chlorine by monitoring the absorption due to the complex at 355 nm in acetonitrile as a function of the TMAC concentration using **1** as a source for chlorine atoms. As can be seen from Figure 5, the absorption due to the complex does not reach a plateau even for the highest achievable TMAC concentration (~20 mM). Thus, the theoretically expected absorbance for the case of quantitative trapping was calculated as follows:

The quantum yield for Φ_{tr}, the trapping of chlorine atoms by chloride, is

$$\Phi_{tr} = \frac{k_1[\mathrm{Cl}^-]}{(1/\tau_0) + k_1[\mathrm{Cl}^-]} \tag{6}$$

where k_1 is the rate constant for reaction 1 (vide supra) and τ_0 is the lifetime of chlorine atoms in the absence of chloride. The absorbance at 355 nm is a linear function of the quantum yield of trapping, i.e., $\Phi_{tr} = a\mathrm{OD}_{355}$, a being a constant that includes both experimental parameters and the quantum yield of chlorine atom formation. Thus, eq 6 can be rewritten as

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$$\frac{1}{\mathrm{OD}_{355}} = a + \frac{a}{\tau_0 k_1[\mathrm{Cl}^-]} = a + \frac{b}{[\mathrm{Cl}^-]} \qquad (7)$$

Using this expression, we were able to extrapolate the observed absorptions to infinite chloride concentration by fitting the data to eq 7 (Figure 5) and thereby to correct the observed quantum yield for that fraction of chlorine atoms that was not trapped by chloride under the conditions of our experiments (8 mM TMAC). From the obtained values of *a* and *b* and the value for k_1 in acetonitrile, the lifetime of chlorine atoms under our experimental conditions is calculated to be $\tau_0 = 45$ ns in acetonitrile in the presence of 0.003 M **1**.

Due to the interference with other signals (vide supra) neither the chloride nor the benzene complex could be used to determine $\Phi_{\mathrm{Cl}\bullet}$ for **2** and **3**. Thus, solutions of **2** and **3** in diglyme were irradiated under steady-state conditions, and the quantum yields of HCl formation were determined by acid−base titrations. To ensure that chlorine atoms were trapped quantitatively by hydrogen abstraction to yield HCl, diglyme instead of acetonitrile was used as solvent, since acetonitrile is a poor hydrogen donor.[25] We also determined Φ_{HCl} of **1** under steady-state conditions to verify whether the values obtained by the two different methods are consistent. The quantum yields are summarized in Table 1. We believe that these values reflect that **1** photodissociates about 30−40 times more efficiently than **2** and **3**, which is in qualitative agreement with the transient spectra obtained in the presence of TMAC and benzene. $\Phi_{\mathrm{Cl}\bullet}(\mathbf{1})$ is not affected by oxygen. This observation is consistent with the lack of triplet quenching observed for **1**. The quantum yields of **2** and **3** can be taken as being the same within the experimental error (±20%). This is not surprising given the structural similarity and the comparable S_1 energy.

Finally, the quantum yields obtained using the laser system and the steady-state irradiation agree well, indicating that the quantum yield of chlorine atom formation can be approximated by the quantum yield of HCl generation.

Given that the S_1 and T_1 states are responsible for the photodissociation of **1**−**3** the difference in the quantum yields for photodissociation is probably due to the lower excitation energy of these states of **2** and **3** relative to **1**. However, the quantum yield depends not only on the rate constant of photocleavage but also on the rate constants of all the other processes that deactivate the photoreactive state. Thus, the lower quantum yield of **2** and **3** may also reflect the fact that these states are more effectively deactivated by nondissociative processes in **2** and **3** compared to **1.** The lack of photophysical data for the triazine chromophore and the fact that the S_1 and T_1 states of **1**−**3** cannot be observed directly with our spectroscopic techniques would make additional interpretation highly speculative.

It should be noted that the photodissociation studied here is of the same type as the carbon−halogen bond cleavage of arylmethyl halides, a reaction that has been investigated in detail for a long time.[26−31] These systems are usually easier to study since they exhibit longer intrinsic lifetimes for both the S_1 and T_1 states, i.e., both states are emissive and can be observed directly. The main result derived from these studies is that in aprotic solvents these compounds undergo exclusively homolysis leading to radicals but heterolysis *and* homolysys in protic solvents. However, several different mechanisms regarding the multiplicity of the photoreactive state(s) and how they govern the sensitive balance between the two pathways have been postulated, none of which has been shown to be unambiguously true. Therefore, these studies are of little value in order to elucidate the multiplicity of the photoreactive state for the triazine system studied here.

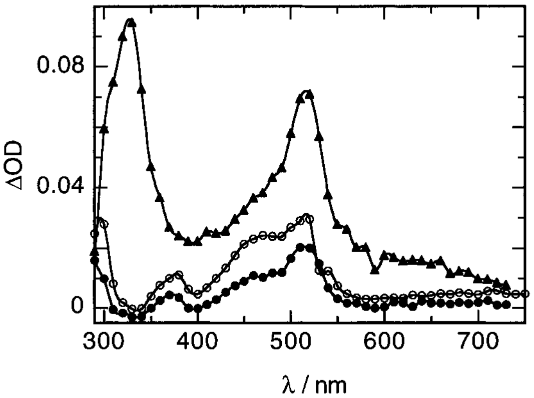

Figure 6. Transient spectrum recorded following 308-nm laser excitation of ACPT in deaerated (▲) and oxygen-saturated (●) acetonitrile. The third spectrum (○) was obtained following 355-nm excitation of ACPT in deaerated acetonitrile in the presence of 0.001 M **1**.

Indirect Excitation Using Phenothiazines as Sensitizers. *Laser Flash Photolysis.* The phenothiazine derivatives used as photosensitizers in this work and the abbreviations are listed in Chart 2. For all of these molecules laser excitation at 308 nm in deaerated acetonitrile led to transient absorptions due to two different transients. The more intense one had lifetimes that were typically 1−2 μs and was efficiently quenched by oxygen. The second transient decayed more slowly and was found to be insensitive to oxygen. Analogous observations have been reported before for these compounds,[7] and the short-lived transient has been assigned to the triplet state of these phenothiazine sensitizers, while the residual absorption has been attributed to the radical cation. The radical cation can be formed even in the absence of an electron acceptor and has been attributed to self-quenching that is believed to involve a small yield of charge transfer. The transient spectra obtained for ACPT in deaerated and oxygen-purged acetonitrile are shown in Figure 6. The spectral data for all of these compounds are included in Table 2. The data agree well with those reported in diglyme.[7]

On the basis of these observations, we conclude that the primary photochemical step of the interaction

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(25) For example, the rate constant for hydrogen abstraction of acetone from acetonitrile is reported to be $k_q < 10^3$ M^{-1} s^{-1}, whereas for methanol and cyclohexane the values are 10^5 and 3×10^5 M^{-1} s^{-1}, respectively: Turro, N. J. In *Modern Molecular Photochemistry*: Benjamin Cummings; Menlo Park, CA, 1978; p 374.

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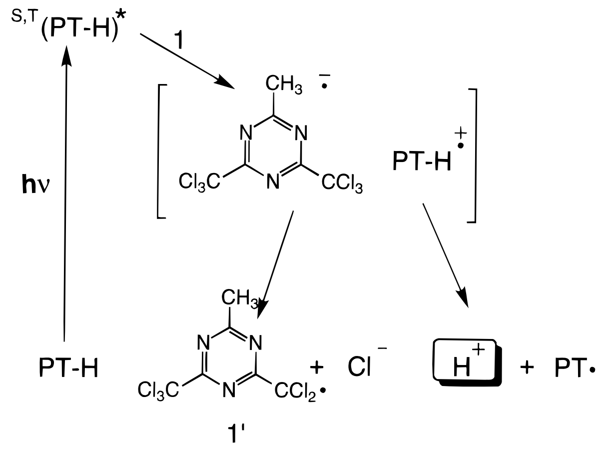
Table 2. Excited-State and Redox Properties of the Sensitizer Used (All Data in Acetonitrile at Room Temperature, unless Stated Differently)

sensitizer	T–T absorption λ_{max}/nm	residual[a] absorption λ_{max}/nm	$E^{\circ\prime}$ [b] (V)	E_T[b] (eV)	ΔE_T (V)	fluorescence λ_{max}/nm	τ_S (ns)	ΔE_S[b,c] (V)
PT	450	510	0.24	2.60	2.36	442	0.84	2.85
NMPT	470	510	0.38	2.70	2.32	443	1.47	2.81
MEPT	480	550	0.19	2.64	2.45	445	0.89	2.87
ACPT	330	510	0.32	$<$2.32	$<$0.60	565	1.27	2.65
BAPT	350	620	0.18	1.99	1.81	509	26.43	2.57

[a] Due to the radical cation. [b] Data from ref 4. [c] In diglyme.

Scheme 2



between PAGs **1**–**3** and the phenothiazine derivatives is electron transfer from the excited photosensitizer to the triazine as exemplary shown for PAG **1** and phenothiazine in Scheme 2. An electron-transfer mechanism has been proposed to be operational for a triazine-dye system using merocyanine dyes as photosensitizer.[6] This assumption was made on the basis of the redox potentials of the triazine/dye pairs and the observed fluorescence quenching of the dyes by the triazines. Furthermore, Barra et al.[7] showed that the quenching of phenothiazines by 1,3,5-tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione, a PAG yielding HBr upon irradiation, involves electron transfer as the primary process.

The transient spectra of the phenothiazines in nitrogen-purged acetonitrile following laser excitation at 355 nm in the presence of 10^{-3} M of **1** are markedly different from the spectra recorded in the absence of **1**. The intense absorption due to the triplet state is not observable under these conditions, and the transient spectra detected correspond essentially with those measured in oxygen-purged acetonitrile, i.e., the radical cation spectra (see Figure 6). This confirms that the triplet state of these compounds is quenched by electron transfer from the excited phenothiazine to **1**. We preferred 355 nm over 308 nm for laser excitation because **1** does not absorb significantly at this wavelength, ensuring the exclusive excitation of the sensitizer.

Qualitatively analogous results were obtained when **2** or **3** were used as quenchers. In these experiments the samples were excited at 308 nm since the extinction coefficient of **2** and **3** at 308 nm is lower than at 355 nm.

A common feature of all the transient spectra obtained for these sensitizers in the presence of **1** is the formation of another transient observable in the spectral region between 500 and 310 nm. An example is shown in Figure 7 for the transient spectra of BAPT in the presence of 0.001 M **1** in acetonitrile, recorded at various delays after laser excitation. In the spectral region between 500 and 700 nm, the observable signal is clearly a decay and is due to the radical cation, but below 500 nm the kinetics of this signal starts to change due to the interference with the signal from a second transient. For the following reasons, we attribute this signal to the radical **1′**:

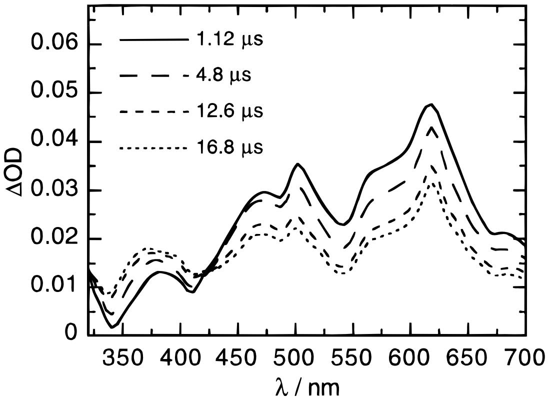


Figure 7. Transient spectra recorded at different time intervals after 355 nm laser excitation of BAPT in deaerated acetonitrile in the presence of 0.001 M **1**.

(1) Qualitatively the same observation is made for all the phenothiazines used, i.e., the formation of this transient must be due to the interaction of **1** with the sensitizers.

(2) The signal cannot be due to the immediate product of **1** in the electron-transfer reaction, the radical anion of **1** since that species should show the same growth kinetics as the radical cation of the sensitizers, i.e., its formation should be instantaneous. Furthermore, the phenothiazine radical cation cannot be involved since the decay of the radical cation does not match the growth kinetics of the new species.

(3) The growth follows first-order kinetics, and the first-order rate constant is found to be in the same range for all of the sensitizers ($k = (8–20) \times 10^4\ \mathrm{s}^{-1}$).

(4) The transient is observable in a spectral region that matches the spectrum of **1′**, already obtained upon direct excitation of **1**.

Quenching Rate Constants. The rate constants for triplet quenching of the phenothiazines by **1**–**3** were determined by monitoring the triplet decay rate constant as a function of quencher concentration; a representative plot for ACPT is shown in Figure 8. The rate constants determined are listed in Table 3; they can be summarized as follows:

(1) The three triazines studied in this work quench the triplet states of the phenothiazines very effectively. The value for MEPT/**1** comes close to the diffusional

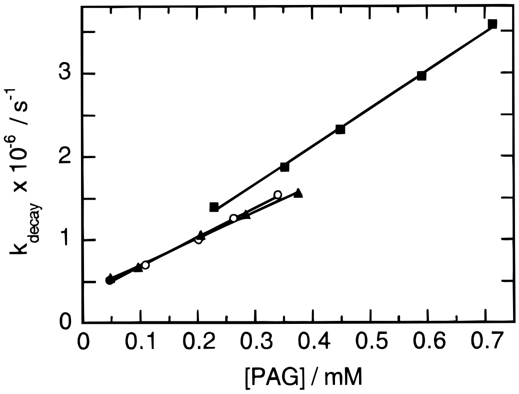


Figure 8. Plot of the observed triplet decay constant for ACTP as a function of the concentration of **1** (■), **2** (○), and **3** (▲) in nitrogen-saturated acetonitrile.

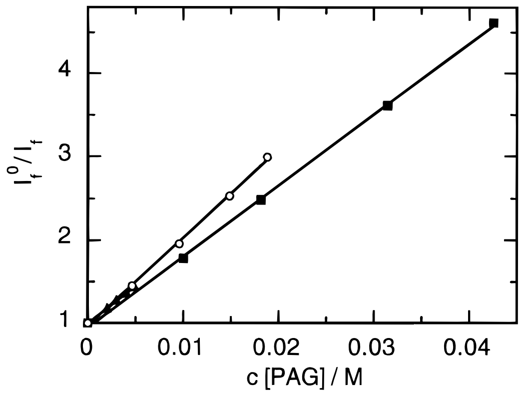


Figure 9. Stern−Volmer plot for the quenching of the fluorescence emission from ACPT by **1** (■), **2** (○), and **3** (▲) in air-saturated acetonitrile.

Table 3. Rate Constants for Triplet Sensitizer Quenching by Triazines 1−3 in Deaerated Acetonitrile at Room Temperature

sensitizer	k_q (**1**)/ 10^9 M^{-1} s^{-1}	k_q (**2**)/ 10^9 M^{-1} s^{-1}	k_q (**3**)/ 10^9 M^{-1} s^{-1}
MEPT	11.9	10.2	8.9
PT	9.0	6.2	6.7
NMPT	6.7	5.0	6.0
BAPT	9.9	12.2	15.9
ACPT	4.5	3.2	3.1

Table 4. Rate Constants for Fluorescence Quenching of Phenothiazine Sensitizers by Triazines 1−3 in Air-Saturated Acetonitrile at Room Temperature

sensitizer	k_q (**1**) / 10^{10} M^{-1} s^{-1}	k_q (**2**)/ 10^{10} M^{-1} s^{-1}	k_q (**3**) 10^{10} M^{-1} s^{-1}
MEPT	4.6		
PT	4.2		
NMPT	4.4		
BAPT	1.3	1.7	1.1
ACPT	6.7	8.3	7.1

limit for acetonitrile (2 × 10^{10} M^{-1} s^{-1}). The rate constants obtained in this study exceed those determined in an earlier study[7] for diglyme and 1,3,5-tris-(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione as quencher by approximately 2 orders of magnitude.

The rate constants correlate well with the difference $\Delta E_T = E_T(x\mathrm{PT}) - E^{o\prime}[x\mathrm{PT}^{+}/x\mathrm{PT}^{0}]$ (Table 2, $E^{o\prime}[x\mathrm{PT}^{+}/x\mathrm{PT}^{0}]$ being the oxidation potential and E_T the triplet energy of the phenothiazines), except for BAPT that exhibited unusually high values. We had to use the parameter ΔE_T instead of the free energy for electron transfer ΔG_{ET} due to the lack of available data for the reduction potentials of the triazines. However, for a given triazine ΔE_T differs from ΔG_{ET} only by a constant, and therefore it is still a measure for the feasibility of electron transfer. The observed correlation between the quenching rate constants and ΔE_T supports the conclusion that the quenching process is an electron transfer from the excited phenothiazine to the triazine.

(2) For a given phenothiazine the triplet state is quenched most efficiently by **1**, while the rate constants of **2** and **3** can be taken as being the same within the experimental error (±15%). This probably reflects the difference in the reduction potentials of **1** compared to **2** and **3**, but contributions from the other parameters that determine k_{ET} (changes in the reorganization energy and the electronic coupling) cannot be ruled out.

The rate constants for singlet state quenching in aerated acetonitrile were obtained from a combination of static, Stern−Volmer type experiments (i.e., the fluorescence intensity was monitored as a function of quencher concentration; see Figure 9) and time-resolved experiments. The fluorescence lifetimes were determined using a picosecond laser with a ~30 ps pulse for excitation, and a streak camera for fluorescence detection. The fluorescence properties of the phenothiazines are included in Table 2. They show close resemblance with those reported before in diglyme,[7] except for ACPT that has been reported to exhibit a very weak fluorescence, a singlet lifetime of 11 ns and $\lambda_{max} = 532$ nm for the fluorescence emission, whereas we found it to be moderately fluorescent with $\tau_f = 1.27$ ns and $\lambda_{max} = 562$ nm in acetonitrile.

To ensure selective excitation of the sensitizer the excitation wavelength in the steady-state experiments using **1** as a quencher was 380 nm for all phenothiazines and 480 nm for ACPT and BAPT when **2** and **3** were used. In the case of PT, MEPT, and NMPT it was impossible to find a wavelength that allows selective excitation of only the phenothiazines when using **2** and **3** as a quencher.

The ${}^1k_q$ values listed in Table 4 all exceed 1 × 10^{10} M^{-1} s^{-1}. Thus, the quenching process is almost diffusion controlled for all the donor/acceptor pairs studied. This is probably the reason that except for BAPT all values are greater than the theoretical limit imposed by diffusion in acetonitrile. It is known that the Stern−Volmer equation is not valid if the rate constant of the observed quenching process approaches the diffusional limit and the intermediate involved is very short lived, yielding values that are too high.[32−34] Due to this effect it is difficult to discuss these values, but they seem to correlate in a similar manner with the difference $\Delta E_S = E_S - E^{o\prime}[x\mathrm{PT}^{+}/x\mathrm{PT}^{0}]$ (see Table 2) as ${}^3k_q$ and ΔE_T .

It should be mentioned that a high rate constant for excited-state quenching does not necessarily equal a high efficiency of photoacid generation. Preliminary experiments have shown that the quantum yield of acid formation using NMPT as a sensitizer is about 2 orders of magnitude smaller than the values for the other phenothiazine derivatives using **1** as an electron acceptor. This is attributed to the fact that the pK_a value of the NMPT radical cation is probably significantly higher

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compared to the other sensitizers since NMPT does not possess a hydrogen atom at the 9-position.

Conclusion

Laser photolysis of all three triazines in acetonitrile leads to formation of chlorine atoms, clearly indicating that the primary photochemical step in the photolysis of these triazines upon direct excitation is the homolytic cleavage of one of the carbon−chlorine bonds, yielding a radical pair. The highly reactive chlorine atom formed in this reaction abstracts a hydrogen atom to form hydrogen chloride. The quantum yield of this photodissociation depends strongly on the excitation energy of the PAG, i.e., extending the sensitivity of the triazine in the visible range of the spectrum also lowers the effectiveness of photoacid generation.

After laser excitation of any of the photosensitizers in the presence of the triazines the respective radical cation and, in the case of the methyl substituted triazine derivative, also the radical **1′** (see Scheme 2) could be detected. This confirms that the primary photochemical step after excitation for the phenothiazine/triazine system is electron transfer from the excited photosensitizer to the triazine. The triazine radical anion stabilizes itself by losing a chloride anion which eventually yields the same radical that is formed upon photocleavage after direct excitation (Scheme 1). From the high quenching rate constants of excited-state quenching we conclude that, except for NMPT, the efficiency of photoacid generation of all the investigated sensitizers may be high enough to be useful in photoresist applications when used in combination with these triazines. However, to determine the versatility of certain sensitizer/triazine systems in detail, it is necessary to determine the quantum yield of acid generation in the actual polymer matrix; this will be dealt with in a subsequent paper.

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