

Ionic vs Free Radical Pathways in the Direct and Sensitized Photochemistry of 2-(4'-Methoxynaphthyl)-4,6-bis(trichloromethyl)-1,3,5-triazine: Relevance for Photoacid Generation

G. Pohlers,[†] J. C. Scaiano,^{*,†} E. Step,[‡] and R. Sinta[‡]

Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada, and Research and Development Laboratories, Shibley Company, 455 Forest Street, Marlborough, Massachusetts 01752-3092

Received September 21, 1998

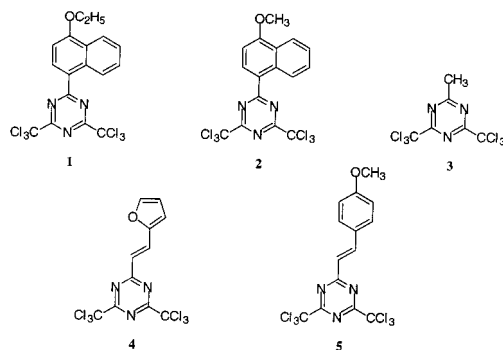
Abstract: The photochemistry and photophysics of the title compound (**2**), which finds application as a photoacid generator in photoresist formulations, has been investigated using a combination of laser flash photolysis work and emission spectroscopy, as well as evaluation of acid formation. The studies were carried out in polar (acetonitrile) and nonpolar (cyclohexane, benzene) solvents, employing both direct excitation and sensitized conditions using isopropylthioxanthone (ITX) and acetone as sensitizers. In nonpolar medium, photolysis of **2** follows a conventional mechanism involving C–Cl cleavage. In contrast, direct excitation of **2** in acetonitrile leads to C–Cl heterolysis with formation of the cation, which can be readily identified by its rapid quenching by nucleophiles such as halide anions, azide, and methanol. Interestingly, **2**⁺ must rearrange for its spectroscopic and kinetic parameters to be consistent with carbocation structures. Several possible structures are proposed for **2**⁺ and its rearranged isomers. Photolysis of **2** in the presence of ITX or acetone also leads to the carbocation, but the yields increase by more than 1 order of magnitude, indicating a higher efficiency of the triplet reaction compared to the singlet reaction. No evidence for electron transfer between **2** and ITX could be found; i.e., the sensitization is entirely due to T–T energy transfer. The quantum yield of HCl generation upon direct excitation (monitored in the microsecond time scale) is very low (0.007); sensitization increases it to 0.111 (acetone) and 0.074 (ITX). In nonpolar solvents, the primary photochemical step in the direct photolysis of these compounds is the homolysis of one of the carbon–chlorine bonds; the chlorine atoms formed in this reaction can be detected by complexation with benzene. Contrary to the ionic pathway, the quantum yield of the homolysis is rather insensitive to sensitization.

Introduction

Only very few studies on the photochemistry of (halomethyl)-1,3,5-triazines upon direct excitation or under sensitized conditions have been published. Buhr et al.¹ studied various 2-substituted 4,6-bis(trichloromethyl)-1,3,5-triazines in solution using direct excitation. One of the compounds, **1** (see Chart 1), is virtually identical to the subject of this work (**2**) and was investigated in detail by preparative photolysis and analysis of the product mixture using a thermospray HPLC/MS setup. In an earlier contribution from this laboratory,² we reported on the photochemistry of **3–5**, which under direct excitation is dominated by C–Cl homolysis. Despite numerous laser photolysis studies of carbocation mechanisms during the past decade,³ little is known about the intermediates that would result from heterolysis of the compounds in Chart 1.

This research was motivated by the rapid developments in microelectronics, which have led to new acid generation techniques in order to keep up with the demand for ever

Chart 1



decreasing feature size. Chemically amplified resists are a substitute for the traditional diazonaphthoquinones (DNQ)⁴-based resists which cannot provide the sensitivity and spatial resolution needed in the fabrication of highest density components. They owe their greatly enhanced sensitivity to a thermally activated, *acid-catalyzed* cross-linking step which results in cross-linking quantum yields greater than 1. Thus, a key element in all these resist systems is a compound that yields an acid as

[†] University of Ottawa.

[‡] Shibley Co.

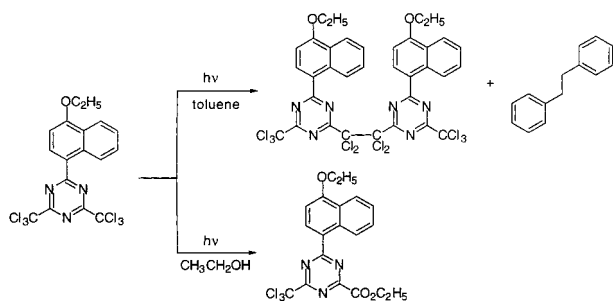
(1) Buhr, G.; Dammel, R.; Lindley, C. R. *Polym. Mater. Sci. Eng.* **1989**, 61, 269.

(2) Pohlers, G.; Scaiano, J. C.; Sinta, R.; Brainard, R.; Pai, D. *Chem. Mater.* **1997**, 9, 1353.

(3) McClelland, R. A. *Spec. Publ.—R. Soc. Chem.* **1995**, 148, 301.

(4) Reiser, A. *Photoreactive Polymers: The Science and Technology of Resists*; John Wiley and Sons: New York, 1989; p 409.

Scheme 1



one product of photolysis, a so-called photoacid generator (PAG). A wide range of acids can be generated by a variety of PAGs, including carboxylic acids, sulfonic acids, hydrogen bromide, and hydrogen chloride. Apart from the interest in molecules such as **1** and **2** reflecting their applications in microlithography, the molecules examined here provide examples of interesting and rather uncommon carbenium ion mechanisms.

An important class of nonionic PAGs for photoacid generation of HCl are (trichloromethyl)-1,3,5-triazines, and many substituted triazines have been reported in the patent literature.⁵ These are usually 4,6-bis(trichloromethyl)-1,3,5-triazines substituted in the 2-position with a suitable chromophore. This chromophore is necessary to induce the bathochromic shift needed to displace the absorption of the unsubstituted compound into the near-UV/visible region of the spectrum, enabling the use of the mercury lamp (365- and 436-nm line) as light source. Even though feature size is not critical in resists operating at these wavelengths, chemical amplification is used to increase the sensitivity of the resist and thereby the throughput. Another way of changing the response range of the PAG is by photosensitization of the triazine using an appropriate sensitizer that absorbs in the spectral region of interest.

Detailed product studies in toluene are in accordance with carbon-chlorine homolysis as a primary step (Scheme 1).¹ This process leads to the free radicals that are ultimately responsible for product formation. In polar protic solvents such as methanol, both the free radical products and some which revealed a contribution from a heterolytic pathway were detected. The key reaction products of the photolysis of **1** in ethanol/ethyl acetate are shown in Scheme 1.¹

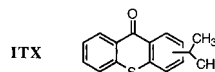
The detailed report by Buhr et al. on **1** and several related compounds did not include any sensitization studies.¹ Kawamura and Matsumoto⁶ have performed experiments employing merocyanine dyes as photosensitizers for 2,4-bis(trichloromethyl)-1,3,5-triazines. Quenching of the dye fluorescence by the triazines was attributed to electron transfer from the excited dye to the triazine.⁶ Since both studies employed rather indirect techniques, we tried in an earlier study² 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. Therefore, we explored the utility of the three 4,6-bis(trichloromethyl)-1,3,5-triazines (**3–5**) as PAGs for HCl generation upon direct excitation and using phenothiazines as photosensitizers for these triazines. It was found that direct excitation in acetonitrile leads to bond homolysis, followed by hydrogen abstraction by the chlorine atoms formed to yield HCl. Sensitization involves electron transfer from the pheno-

thiazine to the triazines and subsequent loss of a chloride by the triazine radical anion and loss of a proton from the phenothiazine radical cation, thus also resulting in HCl formation.²

In this study, triazines **2** and **3** were used in conjunction with isopropyl thioxanthone (ITX, mixture of 2- and 4-isomers frequently employed in industry). The methoxynaphthyl derivative (**2**) was chosen because it has found use in a number of imaging applications which use the broad band illumination of a high-pressure mercury lamp or filtered radiation greater than 365 nm. Compound **3** serves as a model triazine. ITX was chosen as a typical long-wavelength sensitizer that has been employed in both radical and acid generating photochemical schemes. In addition to its relevance for microlithography, the photochemistry of **2** reveals interesting carbocation pathways involving both the triazine and naphthalene moieties.

Experimental Section

Materials. The triazines shown in Chart 1 were purchased from Panchim S.A., France. Compound **2** was purified by recrystallization from dioxane (2 \times) and subsequent sublimation. The triazine **3** was recrystallized from methanol. The purity of the triazines **2** and **3** was checked using melting points and NMR spectroscopy. The melting points determined for **3** (96–98 °C) and **2** (182–184 °C) were virtually identical with those reported in the literature (**3**, 96–97 °C; **2**,¹ 181.5–183 °C). The NMR spectra were in complete agreement with the structure of the compounds; no impurities could be detected. ITX (from Aldrich) was recrystallized twice from methanol/dichloromethane and finally sublimed.



Coumarin 6 (Aldrich) was recrystallized twice from cyclohexane/toluene, tetrabutylammonium chloride (TBAC) was from Fluka, and di(4-*tert*-butylphenyl)iodonium heptafluoropropyl sulfonate (DPHS) was from Shipley. 1-Methoxynaphthalene (MN), chloranil (CA), anthracene (AN), acetone, and TEMPO were obtained from Aldrich. MN was purified by fractional distillation, TEMPO was sublimed prior to use, and CA was recrystallized twice from toluene. All solvents were from BDH (OmniSolv grade) and used as received; the water content of the acetonitrile was 0.004–0.0046% according to the manufacturer.

General Techniques. Absorption spectra were recorded using a Varian CARY-1E spectrophotometer. Emission 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 and low-temperature fluorescence experiments were performed at 77 K (EtOH/MeOH 4:1 glass) using a quartz dewar and 5-mm NMR sample tubes. The theoretical calculations were performed on a Silicon Graphics Indigo workstation using Spartan version 4.04 GL. The semiempirical molecular orbital method of AM1 was selected, if not otherwise stated, using restricted Hartree-Fock (RHF) for all systems.

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. The third harmonic of a Surelite Nd:YAG laser (~6 ns pulse width, ≤ 20 mJ/pulse) was used for 355-nm excitation. 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.^{7,8}

To acquire the transient spectra, a flow system (a 7- \times 7-mm Suprasil quartz flow cell that is connected to a reservoir with Teflon tubing)

(5) Monroe, B. M.; Weed, G. C. *Chem. Rev.* **1993**, *93*, 435.

(6) Kawamura, K.; Matsumoto, H. In *45th Annual Conference of the Society for Imaging Science and Technology*, East Rutherford, NJ; Society for Imaging Science and Technology: Springfield, VA, 1992; p 337.

(7) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

(8) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

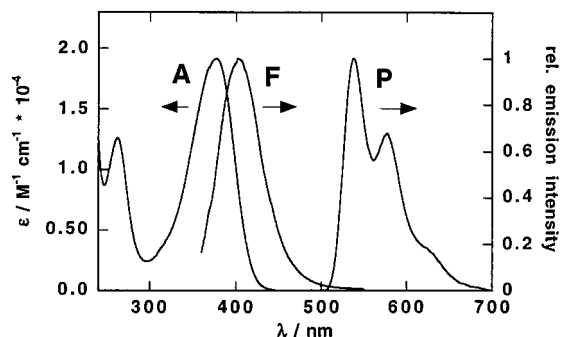


Figure 1. Absorption (A), fluorescence (F), and phosphorescence (P) spectra of **2** in acetonitrile at room temperature (A) and EtOH/MeOH (4:1) at 77 K (F, P), respectively.

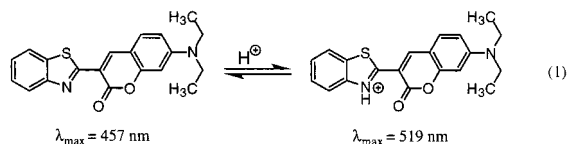
Table 1. Excited State Energies and Triplet Lifetimes of **2**, **3** and the Sensitizers

compound	E_S (kcal mol ⁻¹)	E_T (kcal mol ⁻¹)	τ_T (μ s)
2	73.5 ^a	53.1 ^a	<i>b</i>
3	87 ^c	80 ^c	<i>b</i>
ITX	78 ^f	62.6 ^a	60 ^d
acetone	84 ^f	78 ^f	50 ^{d,e}

^a In a MeOH/EtOH glass at 77 K. ^b Not determined. ^c Estimated (see ref 2). ^d In acetonitrile. ^e Reference 15. ^f Reference 33.

was used. The quenching experiments were carried out in 7- × 7-mm Suprasil quartz cells sealed with a septum. Unless otherwise stated, all samples were deaerated by bubbling with oxygen-free nitrogen for 15 min.

Determination of Quantum Yields of Acid Production. We used the laser flash technique recently developed in this group to determine the quantum yields of acid generation of **2**.⁹ It uses the difference in the absorption spectra of the neutral and protonated forms of Coumarin 6 (C6, reaction 1) to monitor the amount of acid produced upon irradiation of the PAG of interest and the PAG that serves as actinometer.



The dye concentration used was 3×10^{-5} M, and the actinometer was triazine **3** ($\Phi_{\text{HCl}} = 0.40$). A more detailed description of the technique has been given elsewhere.⁹

Results and Discussion

Photophysics. The absorption (A), fluorescence (F), and phosphorescence (P) spectra of **2** are shown in Figure 1. Compound **2** was found to be nonfluorescent in either acetonitrile or cyclohexane at room temperature. Fluorescence and phosphorescence of **2** were observed at 77 K in an ethanol/methanol glass; the calculated singlet and triplet energies obtained from these spectra are summarized in Table 1. Triazine **2** absorbs at significantly longer wavelengths than each of the two subunits it consists of; the longest wavelength bands of MN and **3** are located at 315 ($\epsilon = 2200 \text{ M}^{-1} \text{ cm}^{-1}$) and 270 nm ($\epsilon = 490 \text{ M}^{-1} \text{ cm}^{-1}$), respectively, in contrast to 377 nm ($\epsilon = 20\,000 \text{ M}^{-1} \text{ cm}^{-1}$) for **2**. While the band is broad and structureless in acetonitrile, in cyclohexane a vibrational structure appears (not shown). The transient absorption spectrum of an equimolar mixture of 1-methoxynaphthalene and **3** in acetonitrile taken after laser excitation at 308 nm shows the characteristic features of the 1-methoxynaphthalene radical

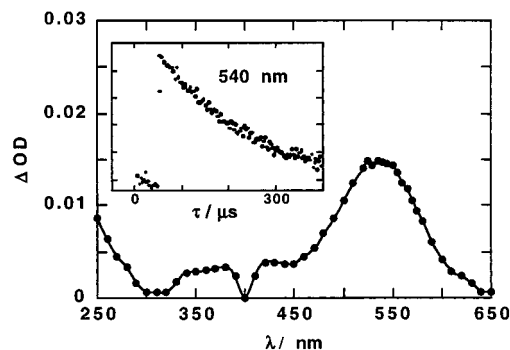


Figure 2. Transient spectrum recorded following 308-nm laser excitation of 0.2 mM **2** in deaerated acetonitrile. Inset: Decay of the signal at 540 nm (attributed to $2^+/\dot{7}^+$) under the same conditions.

cation (spectrum not shown), indicating the feasibility of an electron transfer between the two moieties in acetonitrile. Formation of the radical cation by photoionization of the MN can be ruled out since laser excitation of 1-methoxynaphthalene alone under the same conditions leads to formation of the triplet state of MN. From these results, it is inferred that the 377-nm band of **2** is due to an intramolecular CT transition from the electron-rich methoxynaphthalene moiety to the bis(trichloromethyl)-triazine moiety, which acts as electron acceptor. This is further supported by the finding that the lowest excited singlet state of a related donor-acceptor-substituted triazine, 2-(4-*N,N*-diethylaminophenyl)-4,6-dichloro-1,3,5-triazine, has been shown to be a twisted intramolecular charge-transfer state.¹⁰

Laser Flash Photolysis in Acetonitrile. (i) Transient Absorption Spectra upon Direct Excitation. The transient spectrum recorded after 308-nm laser excitation of **2** in deaerated acetonitrile is shown in Figure 2. It should be noted that the spectral region below 420 nm is distorted due to ground-state bleaching of **2**. At low laser dose (attenuation of the laser output to 10%), the decay of this transient, monitored at 540 nm (see inset in Figure 2), follows clean first-order kinetics ($k = 5.8 \times 10^3 \text{ s}^{-1}$), whereas traces obtained without attenuation could not be satisfactorily fitted to a first-order decay, presumably due to some second-order contributions due to back reaction with chloride ions. On a faster time scale, the formation of this transient ($k = 1.3 \times 10^7 \text{ s}^{-1}$) can also be observed. A plot of absorbance at 540 nm versus laser power yielded a straight line, indicating the monophotonic formation of the transient. The intensity, lifetime, and shape of the transient are not affected by oxygen, whereas its rate of formation increases slightly to $k = 1.9 \times 10^7 \text{ s}^{-1}$. High concentrations (0.5 M) of nucleophilic solvents such as methanol or THF do not affect the growth rate but decrease the yield and lifetime of the transient, and in pure methanol the transient is not observed at all. Furthermore, the signal is quenched by nucleophiles such as chloride ($k_q = 7.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), bromide ($k_q = 8.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, both added as tetrabutylammonium salts), and azide (sodium salt, $k_q = 9.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), i.e., with rate constants close to the diffusional limit in acetonitrile. These values were obtained from plots of the observed rate constant of decay at 540 nm versus the concentration of the respective anion; the estimated error of these and the other rate constants determined in this work is $\pm 20\%$. Based on these results, the band at 540 nm could be due to either the cation 2^+ , formally obtained by heterolysis of one of the carbon-chlorine bonds in **2**, or the radical cation of **2**.

To assign this transient, we tried to specifically generate the radical cation of **2** by photosensitized electron transfer and

(9) Pohlers, G.; Scaiano, J. C.; Sinta, R. *Chem. Mater.* **1997**, *9*, 3222.

(10) Cowley, D. J.; Pasha, I. *J. Chem. Soc., Perkin Trans. 2* **1981**, 918.

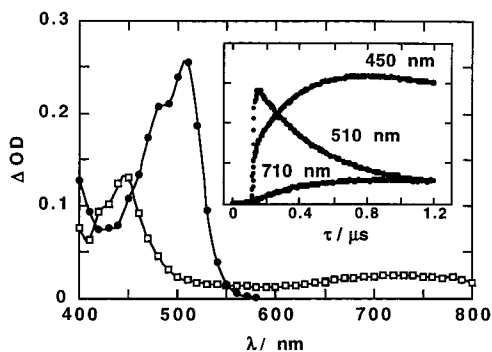
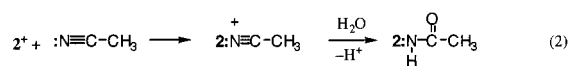


Figure 3. Transient spectrum recorded following 308-nm laser excitation of 3.6 mM CA in deaerated acetonitrile without (●) and with (□) 0.2 mM **2**. Inset: Decay of the signal at 510 (with **2**), 450, and 710 nm (with **2**) under the same conditions.

compare the spectrum obtained with that in Figure 2. The electron acceptor used was chloranil (CA), which has been shown to be an efficient generator for radical cations.¹¹ Excitation (308 nm) of 3.6 mM CA in acetonitrile leads to the formation of triplet CA (Figure 3), with a maximum at 510 nm. Under the same conditions but in the presence of 0.2 mM **2**, the lifetime of the triplet is shortened, and the spectrum exhibits two new bands, one of which (450 nm) is due to the radical anion of chloranil, indicating an electron transfer from **2** to the triplet chloranil. Since the chloranil anion has no absorption at wavelengths greater than 550 nm,¹¹ the second band at 720 nm in Figure 3 must be due to the radical cation of **2**. This is supported by the finding that the two bands at 450 and 720 nm show virtually the same growth kinetics ($k_{450 \text{ nm}} = 4.8 \times 10^6 \text{ s}^{-1}$, $k_{710 \text{ nm}} = 4.4 \times 10^6 \text{ s}^{-1}$), matching the decay kinetics of the triplet reasonably well ($k_{510 \text{ nm}} = 3.2 \times 10^6 \text{ s}^{-1}$). It should be noted that no band at 540 nm is observed, even on longer time scales, when the signals due to the CA triplet and the radical anion of CA have already decayed, thereby potentially enabling the observation of the very long-lived 540-nm transient. This, together with the absence of the 710-nm band in Figure 2, leads us to the conclusion that the transient at 540 nm observed upon direct excitation is not due to the radical cation of **2**.

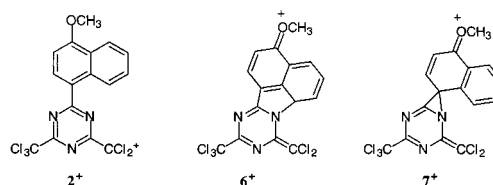
Since it has been established that the signal is due to a cation, one alternative to assigning this transient to **2**⁺ is to assume that the signal is due to a nitrilium ion formed as a result of the addition of **2**⁺ to the solvent, followed by addition of water to yield an amide (reaction 2).



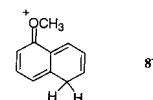
The formation of nitrilium ions as a product of the addition of carbocations to acetonitrile has been established by Steenken et al.,¹² who investigated substituted diphenylmethyl cations by laser flash photolysis. However, they could not observe the absorption of the nitrilium ions directly, but they postulated the formation of such an intermediate on the basis of time-resolved conductivity experiments and the detection of the corresponding amide formed by addition of water. The assignment of the 540-nm band to the nitrilium ion presents problems since the observed growth should represent the addition of **2**⁺ to acetonitrile. The growth at 540 nm takes place with a lifetime of ca. 70 ns, while the addition to better nucleophiles such as methanol

or THF should be much faster. For example, Steenken et al. report the (ClPh)₂CH⁺ cation to add to acetonitrile with a rate constant of $2.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, whereas the rate constant of the addition to THF was $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, i.e., 360 times faster. However, in our experiment in acetonitrile, the presence of 0.5 M THF did not influence the growth kinetics of the 540-nm signal at all. If the growth really reflected the addition of **2**⁺ to acetonitrile, it should have been considerably faster due to the competition between the solvent and the THF. Finally, the fact that Steenken et al. failed to observe any transient absorption due to the nitrilium ion makes it rather unlikely that the signal at 540 nm arises from such a species, because there is no reason why, in our case, it should be more readily detectable.

The structure of **2**⁺ is a matter of concern; its lifetime, its absorption characteristics, and the observation of a short but reproducible delay in its formation are surprising. It is likely that a rearranged form such as **6**⁺ or **7**⁺ is actually the detected species:



Given the observed products (Scheme 1),¹ it seems likely that these species are effectively a *reservoir* for **2**⁺ (i.e., interconversion is reversible), with the carbocation center in **2**⁺ still acting as the reactive center. To check the energetic feasibility for the formation of species **6**⁺ and **7**⁺ from **2**⁺, we calculated the heats of formation for all three cations using the semi-empirical AM1 method. The obtained values are 206 (**2**⁺), 218 (**6**⁺), and 206 kcal/mol (**7**⁺); i.e., **2**⁺ and **7**⁺ are essentially isoenergetic. This points to **7**⁺ rather than **6**⁺ being the detected species and also supports the assumption that the interconversion between the two species is reversible. Further experimental support that the observed transient is, indeed, **7**⁺ and not **6**⁺ comes from the spectrum of the carbocation **8**⁺ produced by protonation of 1-methoxynaphthalene in the 5-position, which shows an absorption maximum at 550 nm, virtually identical to that of **2**⁺.^{13,14}



It should be noted that structure **7**⁺ contains a chromophore very similar to that of **8**⁺, with five conjugated double bonds. **7**⁺ is not planar: its AM1-optimized geometry reveals that the two ring systems are twisted at an angle of 63°, with the positive charge localized in the methoxynaphthalene subunit. This and the fact that conjugation between the triazine and methoxynaphthalene part is impossible due to the sp³-hybridized carbon atom at the 5-position make significant interaction between the two chromophores impossible; i.e., the absorption spectrum of **7**⁺ must be the superposition of the two spectra arising from the triazine and the naphthalene moiety. Therefore, since the triazine chromophore should not have any absorption at wavelengths greater than 500 nm, the spectral similarity between **8**⁺ and the

(13) Mathivanan, N.; Cozens, F.; McClelland, R. A.; Steenken, S. *J. Am. Chem. Soc.* **1992**, *114*, 2198.

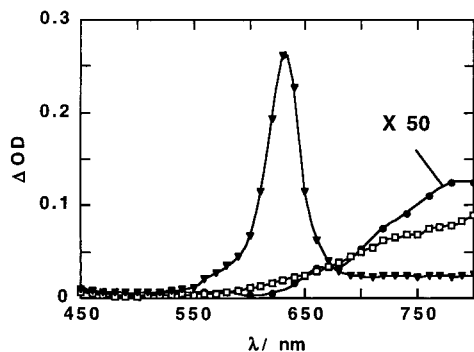
(14) We are grateful to Prof. R. A. McClelland for bringing to our attention this possibility and the similarity between the spectra for **2**⁺ (or **7**⁺) and **8**⁺.

(11) Lew, C. S. Q.; Brisson, J. R.; Johnston, L. J. *J. Org. Chem.* **1997**, *62*, 4047.

(12) Bartl, J.; Steenken, S.; Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918.

Table 2. Quantum Yields for Photoacid Generation of Triazine **2** in Acetonitrile at Room Temperature under Various Conditions (Estimated Error, $\pm 25\%$)

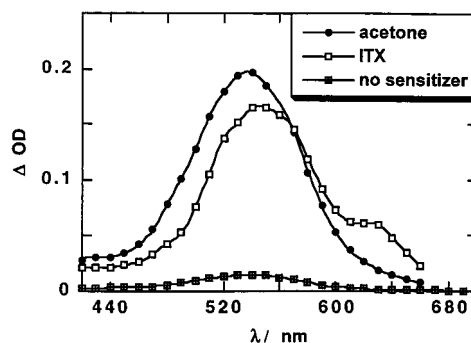
excitation	added quencher	Φ_{acid}
direct	none	0.007
direct	1 M MeOH	0.007
direct	0.5 M TBAC	<0.0001
sensitized (acetone)	none	0.111
sensitized (ITX)	none	0.074
sensitized (acetone)	1 M MeOH	0.108
sensitized (acetone)	0.5 M TBAC	<0.0001

**Figure 4.** Transient spectrum recorded following 308-nm laser excitation of 0.13 mM ITX in deaerated (\blacktriangledown) and oxygenated (\bullet) acetonitrile and in the presence of 1 mM DPHS after 355-nm excitation in deaerated acetonitrile (\square).

cation spectrum of Figure 2 clearly indicates the formation of 7^+ . The same argument cannot be made for structure 6^+ , since here both chromophores are conjugated and almost coplanar. We note that laser flash photolysis techniques measure changes in absorbance (ΔOD) rather than absorbance. Given the strong absorbance of **2** at ~ 370 nm (see Figure 1), one would anticipate a bleaching signal in this wavelength region. The fact that this is not observed requires that the transient formed (i.e., 2^+ or 7^+) absorb strongly in this region. This is consistent with the literature,¹³ which shows that 8^+ has two strong absorptions at 360 and 550 nm. The unusual spectral features in this wavelength region (see Figure 2) suggest that (not surprisingly) the spectral match is not perfect.

(ii) Transient Absorption Spectra under Sensitized Conditions. To study the photochemistry of **2** under sensitized conditions, we used acetone and ITX as sensitizers. We choose acetone as a second sensitizer for this study because it has two advantages over ITX: it is more difficult to oxidize and reduce than ITX, which makes electron transfer an unlikely sensitization pathway, and it does not give rise to intense T–T absorption signals ($\lambda_{\text{max}} = 302$ nm, $\epsilon_{302 \text{ nm}} = 600 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁵ The relevant parameters for the two sensitizers and **2** are collected in Table 2.

To decide whether electron transfer leading to a radical ion pair is involved in the sensitization of **2** by ITX, we tried to generate its radical cation, the spectrum of which has not been reported in the literature. For this purpose, di(4-*tert*-butyl-phenyl)iodonium heptafluoropropyl sulfonate (DPHS) instead of chloranil was employed as electron acceptor; in contrast to CA, DPHS allows exclusive excitation of the ITX at 355 nm, and the radical anion does not give rise to signals in the spectral range of interest that would mask the absorption of the ITX radical cation. The spectra of ITX in acetonitrile with and without 0.001 M DPHS are shown in Figure 4, where the band at 635 nm ($\tau = 60 \mu\text{s}$) corresponds to the ITX triplet. The

**Figure 5.** Transient spectra recorded after 308-nm laser excitation of 0.2 mM **2** in deoxygenated acetonitrile with and without added sensitizers at room temperature.

lifetime of the triplet state is significantly reduced in the presence of DPHS, and a new transient appears, exhibiting a growth kinetics and a maximum at or above 780 nm. The lifetime of this transient is only slightly affected by oxygen, and its growth kinetics monitored at 710 nm matches the decay kinetics of the ITX triplet at 635 nm. Based on these observations, we assign this transient to the radical cation of ITX. This is further supported by the spectrum of ITX alone in oxygen-saturated acetonitrile, obtained after the triplet signal has already decayed (Figure 4), which bears close resemblance to the one obtained with DPHS under nitrogen. We attribute this transient to the ITX radical cation also formed in low yields via photoejection from the ITX. Such direct photoejection has, for example, been observed for phenothiazines.¹⁶ While the detection of radical cations from stabilized ketones is not common, there is precedent in the literature for fluorenone-derived radical cations.¹⁷

Figure 5 shows the spectra obtained after direct and sensitized excitation of **2** using ITX and acetone as sensitizers. The three spectra show the same signal in shape and spectral position; the deviation from the two other spectra observed for ITX in the region > 540 nm is a result of the very intense absorption of the ITX triplet at 635 nm which had not completely decayed in the time window used to record these spectra. The absence of any signals at wavelengths > 700 nm for ITX as sensitizer rules out the formation of the ITX radical cation and electron transfer as a sensitization mechanism. Based on the triplet energies and the observation that **2** quenches the triplet state of ITX with a rate constant of $k_q = 7.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile, we propose that energy transfer from triplet ITX to **2** is the operational mechanism. This is in agreement with the finding that the ITX triplet is quenched by **3** with a much lower rate constant ($k_q = 3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). Triazine **3** has a higher triplet energy than ITX but was found to be a better electron acceptor than **2**.² If electron transfer was involved to a significant degree in the deactivation of the ITX triplet by the triazines **2** and **3**, then **3** should quench with a rate constant higher than or at least equal to that of **2**. But, since triplet energy transfer from ITX to **2** but not **3** is energetically feasible, the quenching rate constant should be much higher for **2** compared to that for **3** if energy transfer is the predominant pathway, as experimentally observed.

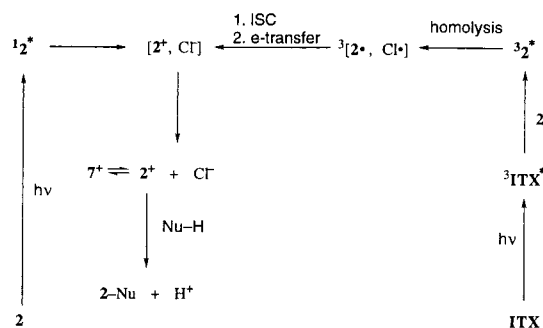
It should be noted that the three spectra in Figure 5 were obtained under identical instrumental conditions, and the sensitizers were added to the same stock solution of **2** in acetonitrile and their absorbances matched; i.e., the differences

(16) Barra, M.; Redmond, R. W.; Allen, M. T.; Calabrese, G. S.; Sinta, R.; Scaiano, J. C. *Macromolecules* **1991**, *24*, 4972.

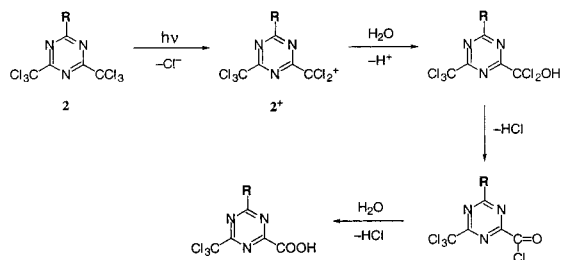
(17) Wang, Z.; McGimpsey, W. G.; Ren, Y.; Weinger, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 7925.

(15) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

Scheme 2



Scheme 3



in the optical density of the bands reflects the different quantum yields of formation of $2^+/7^+$. The concentration of **2** in these experiments was adjusted to ensure that 99% of the ITX and acetone triplets would be quenched by the triazine, based on triplet lifetimes of 60 μs for ITX (this work) and 50 μs for acetone¹⁸ and a minimum triplet quenching rate of $k_q = 7.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, the value determined for ITX/2 under our conditions. The concentrations of acetone and ITX were 0.25 ($\epsilon_{308 \text{ nm}}(\text{acetone}) = 2.7 \text{ M}^{-1} \text{ cm}^{-1}$) and $8.9 \times 10^{-4} \text{ M}$, respectively. If one corrects the signals obtained under sensitized conditions for direct formation of the cation and the absorbance of **2**, the normalized ratio of the intensities at 540 nm are 1:0.83:0.06 for acetone:ITX:no sensitizer. Given an intersystem crossing yield of ~ 1.0 for acetone, this means that the quantum yield of cation formation from the triplet state of **2** is at least 17 times higher than that from the singlet state. This estimation is an upper limit, assuming that all the cation formed upon direct excitation is actually due to the singlet state reaction. It is difficult to verify whether this is the case. The finding that the intensity of the 540-nm band for direct excitation is the same under oxygen or nitrogen indicates either a predominant singlet reaction or a very short triplet lifetime ($\tau \leq 5 \text{ ns}$); the latter is in accordance with the result that we failed to detect the triplet state of **2** with our system, even in the experiments employing a sensitizer, where the triplet state must have been populated. The reduced efficiency of cation formation in the case of ITX as compared to that observed for acetone is attributed to the lower quantum yield of intersystem crossing of ITX.

The reactivity of the triplet state is surprising since it cannot decay directly to a closed-shell system such as an ion pair; i.e., an efficient spin inversion mechanism is required. Similar results have already been observed for the sensitized photodissociation of benzyl halides,¹⁹ and it has been concluded that the primary photochemical step is actually formation of a radical pair via homolysis, followed by electron transfer to form the ion pair.^{20,21} The spin mixing occurs within the geminate radical pair, thereby allowing the formation of ions from the triplet state. We assume

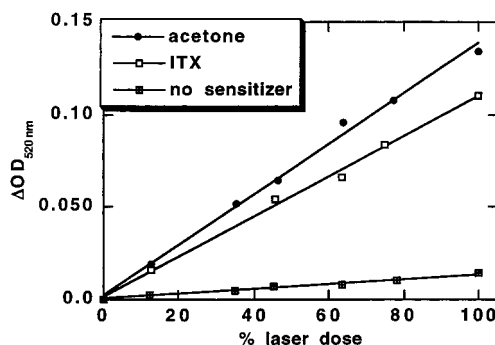


Figure 6. Absorbance of the C6 cation monitored at 520 nm after 308-nm excitation of **2** with and without sensitizers as a function of laser dose in deaerated acetonitrile at room temperature.

that the same mechanism is operational in our case in acetonitrile, as summarized in Scheme 2.

(iii) Quantum Yields of Photoacid Generation. At this point, it seems worthwhile to discuss the possible pathway of Brønsted acid generation from **2** once the cation has been formed. The most probable pathway seems to be the addition of 2^+ to a nucleophile bearing a dissociable proton and subsequent deprotonation of this adduct, as outlined in Scheme 3 (vide infra). This means that the photoacid generation efficiency of **2** should depend on the solvent, being lower in the very weak Lewis base acetonitrile than, for example, in the more nucleophilic methanol. The quantum yields for direct and sensitized photoacid generation of **2** in acetonitrile are shown in Table 2. The values for the sensitizers have been corrected for the acid production via direct excitation and the absorbance of **2**. They were obtained from the slopes of plots such as that in Figure 6, showing the absorbance of the Coumarin 6 (C6) cation at 520 nm obtained after dye protonation following 308-nm laser excitation of **2** with and without sensitization.

The quantum yield of acid generation upon direct excitation is considerably lower than that in the presence of the sensitizers, in accordance with the differences in cation formation efficiency mentioned above. The normalized ratio of the quantum yields of acid generation (1:0.79:0.06) is in very good agreement with the ratio obtained for the cation formation; i.e. $2^+/7^+$ are clearly responsible for the formation of the dye monocation. As expected, in the presence of 0.5 M TBAC, no formation of the monocation of C6 can be detected due to the rapid quenching of $2^+/7^+$ by the chloride ions.

Given the assumed pathway of acid formation as outlined in Scheme 2, the formation of the dye monocation in dry acetonitrile may seem surprising, since acetonitrile is a very weak nucleophile and does not possess a dissociable proton. Of course, one might argue that there is enough residual nucleophile already present in the acetonitrile to trap at least some of the $2^+/7^+$ (or the nitrilium ion) and generate a Brønsted acid, the main nucleophilic contaminant being water. This theory can easily be invalidated by the following considerations: If the residual water in the solvent was really responsible for the observation of the dye cation, the addition of more nucleophile such as methanol must lead to a further increase of the C6 cation absorption, since now a larger fraction of the initially formed amount of 2^+ is trapped. This assumes that the concentration of residual water in the acetonitrile used is too low to quantitatively scavenge all the $2^+/7^+$, even if that low initial water content of the solvent (2 mM) increased slightly during

(18) Porter, G.; Dogra, S. K.; Loutfy, R. O.; Sugamori, S. E.; Yip, R. W. *J. Chem. Soc., Faraday Trans. 1* **1973**, 1462.

(19) Larson, J. R.; Epiotis, N. D.; McMurchie, L. E. *J. Org. Chem.* **1980**, *45*, 1388.

(20) Lipson, M.; Deniz, A. A.; Peters, K. S. *J. Phys. Chem.* **1996**, *100*, 3580.

(21) Dreyer, J.; Peters, K. S. *J. Phys. Chem.* **1996**, *100*, 15156.

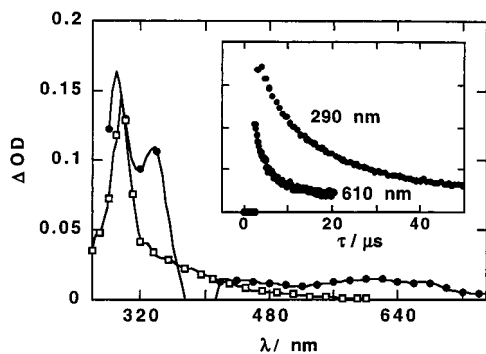


Figure 7. Transient spectra recorded after 308-nm laser excitation of 0.2 mM **2** (●) and 3 mM **3** (□) in deaerated cyclohexane and acetonitrile, respectively. Inset: Decay of the signal at 290 and 610 nm. The data recorded at 610 nm have been multiplied by 10.

sample preparation. This assumption is validated by the finding that a much higher concentration of methanol (1 M), a better nucleophile than water, under the same conditions only increased the decay rate constant of 7^+ by a factor of ~ 2.5 . However, the addition of 1 M methanol as a nucleophile does not increase the quantum yield at all for both direct excitation and sensitization (Table 2). This can only be explained if one assumes that the dye cation observed in pure acetonitrile *cannot* be due to trapping of 2^+ by residual water.

The correct explanation for the formation of the dye monocation in acetonitrile is the direct addition of the Lewis acid 2^+ to the nitrogen atom of C6 in the same manner as a proton. That complex has absorption properties very similar to those of the protonated dye and is responsible for the absorption at 519 nm. Upon addition of 1 M methanol, a fraction of 2^+ is, indeed, trapped by the alcohol, setting a proton free which then protonates the dye. But that fraction is now unavailable to add directly to the dye, and thus the overall absorbance due to the C6 cation remains essentially unchanged. This theory is substantiated by the finding that a solution of C6 in dry acetonitrile turned red upon addition of triphenylcarbenium hexachloroantimonate, a commercially available stable carbenium ion, yielding the absorption spectrum of the C6 monocation as it is obtained by addition of a Brønsted acid. Furthermore, similar results have been obtained with other Lewis acids such as ScOTf, Al(Et)₃, TiCl₄, ZnCl₂, etc. in anhydrous solvents, indicating the feasibility of complexation of C6 by Lewis acids.

It seems very likely that each molecule of **2** eventually leads to three molecules of HCl, as indicated in Scheme 3, and consistent with the observation of carboxylic acid products by Buhr et al.¹ in the case of **1**. However, the kinetic traces obtained in the photoacid generation efficiency experiments do not indicate a stepwise acid production; the absorption due to the protonated C6 at 520 nm reaches a plateau after ~ 50 μ s and does not change up to 2 ms. This result implies that the water adduct to 2^+ is too long-lived for its decay to be monitored with our instrument.

Laser Flash Photolysis in Nonpolar Solvents. The transient spectrum recorded after 308-nm laser excitation of **2** in deaerated cyclohexane shown in Figure 7 is markedly different from that obtained in acetonitrile, having maxima at 290, 340, and 610 nm. The three bands decay with clean second-order kinetics, but the 610-nm band decays faster than the two short-wavelength bands, indicating the presence of two different transients. They are both readily quenched by oxygen, now following a pseudo-first-order decay with virtually the same rate constant ($k = 3.7 \times 10^6$ s⁻¹). To decide whether one of the transients is the triplet state of **2**, which would also be quenched by oxygen, we made

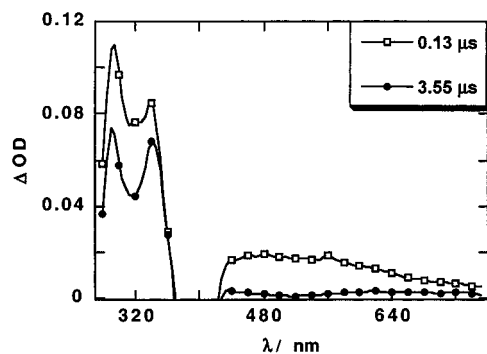
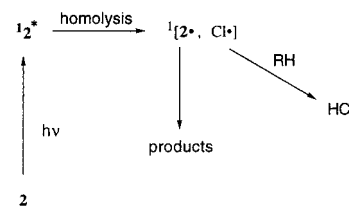


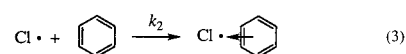
Figure 8. Transient spectrum recorded at different time intervals after 308-nm laser excitation of 0.3 mM **2** in deaerated benzene. Only 50% of the acquired data points are shown.

Scheme 4



an attempt to quench the T₁ state with anthracene, which has a low triplet energy (43 kcal/mol) and a very intense T–T absorption at 425 nm. However, the presence of 4×10^{-4} M anthracene did not result in either a significant lifetime shortening of the 290- or 610-nm transient or detection of anthracene triplet by sensitization. All these results are in agreement with a homolysis of one of the carbon–chlorine bonds, as already observed for triazine **3** in our earlier study, yielding the radical $2^•$ and a chlorine atom, which then abstracts hydrogen from the solvent to form HCl (Scheme 4).

An easy way to validate this mechanism is to establish the formation of the chlorine atoms formed upon photolysis. A way of detecting chlorine atoms is monitoring the CT complex between benzene and Cl[•],²² reaction 3:



This complex ($k_2 = 6 \times 10^9$ M⁻¹ s⁻¹)²³ exhibits two easily detectable bands at 490 and 310 nm. In the region >400 nm, the spectrum from **2** obtained 0.13 μ s after laser excitation at 308 nm in benzene (Figure 8) is in good agreement with the spectrum reported for the complex in the literature,^{22,23} indicating the formation of chlorine atoms. The spectral region below 400 nm is dominated by the two peaks due to the excitation of **2**, masking the 310-nm band of the complex. At longer time scales, when the complex has already decayed, the residual absorption shows close resemblance to that already obtained in cyclohexane. The signal of the complex appeared instantaneously within the time resolution of our system, pointing to a lifetime of the photodissociation below 20 ns. These results confirm the *homolysis* of a carbon–chlorine bond as the primary photochemical step in the photolysis of **2** in benzene and cyclohexane without subsequent electron transfer, in contrast to the ionic pathway observed in acetonitrile.

As already mentioned above, such a delicate balance between homolytic and ionic pathways is not unprecedented for the

(22) Buehler, R. E.; Ebert, M. *Nature* **1967**, *214*, 1220.

(23) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Luszyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5464.

carbon–halogen bond cleavage of arylmethyl halides, a reaction that has been investigated in detail.^{24–29} 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 homolysis occur in protic solvents. 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;^{24–29} none of these has been shown to be unambiguously true. Contrary to the fine balance between homolysis and heterolysis observed for **2**, triazine **3** shows only the homolytic pathway even in polar solvents such as acetonitrile.² This can be understood if one considers that the bis(trichloromethyl)-triazine moiety is a good electron acceptor; this manifests itself in the photoinduced electron transfer from electron donors to **3** as observed in this work (methoxynaphthalene) and in our earlier study with phenothiazines.² A heterolytic pathway for compound **3** would have to result in the formation of the monocation 3^+ ; the ionization potential of **3** is probably too high to make this reaction energetically feasible even in a polar solvent. In **2**, however, the presence of the electron-rich methoxynaphthalene moiety lowers the IP to a level where heterolysis is possible. The rearrangement of the initially formed 2^+ to 7^+ probably reflects the attempt of the system to “make better use” of the electron-donating ability of the methoxynaphthalene moiety, since effective delocalization of the positive charge into the methoxynaphthalene part is difficult in 2^+ .

The assignment of one of the transients to the radical 2^\bullet is not straightforward. For comparison, the spectrum of the corresponding radical 3^\bullet , generated upon photolysis of **3** in acetonitrile, is also shown in Figure 7; it has a maximum at 295 nm, very close to the 290-nm maximum observed for **2**. In another attempt, we tried to assign the two transients via their different quenching rate constants for the trapping with TEMPO, which has been reported to react with carbon-centered radicals with rate constants of $(0.6\text{--}12) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in isooctane,³⁰ the value for the related benzyl radical being $4.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. For the transients derived from **2**, we determined rate constants of 6.9×10^8 (290 nm) and $12.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (610 nm), compared to $8.8 \times 10^8 \text{ M}^{-1}$ for the radical 3^\bullet in cyclohexane (plots not shown). The finding that both the 290- and 610-nm transients are quenched by TEMPO supports that these species are radicals, although TEMPO is known to quench triplet states of organic molecules with triplet energies close to that of **2** (e.g., fluoranthene, $E_T = 52.9 \text{ kcal/mol}$;³¹ $k_q = 4.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$).³² However, this possibility can be ruled out on the basis of the lack of quenching in the experiment using anthracene as triplet quencher. Unfortunately, the quenching rate constant obtained for 3^\bullet falls right between the two values for 2^\bullet , making an unambiguous assignment very difficult. However, the lower value obtained for the 290-nm transient suggests that this band is due to the radical 2^\bullet , since the quenching of carbon-

centered radicals by TEMPO is faster the less stable the radical is.³⁰ There is no reason to believe that the substitution of the methyl group in **3** by the 4-methoxynaphthyl group should lead to a destabilization of 3^\bullet , i.e., to a faster quenching rate constant, as observed for the 610-nm transient.

Transient Absorption Spectra under Sensitized Conditions/Quantum Yields of Acid Formation. In cyclohexane, the 290-nm signal intensity decreases approximately 50% upon addition of 0.10 M acetone, probably due to the filter effect of acetone, whereas the intensity of the 610-nm band increases by a factor of 3. A way of testing whether the acid production is increased by sensitization is to monitor the absorption of the protonated C6 with and without added acetone. In an experiment using 0.1 M acetone, 0.03 mM C6, and 0.2 mM **2** in cyclohexane, the absorbance of the monocation at 520 nm did not change, indicating that there is some sensitized acid generation, since otherwise a decrease in absorbance due to the filter effect of the acetone would be expected. Also, this argues against an assignment of the 610-nm band to radical 2^\bullet , since in this case an increase in acid production comparable to the increase of the 610-nm absorbance of that band should have been detected.

It should be noted, though, that the efficiency of the quenching of the acetone triplet by **2** is significantly reduced in cyclohexane, since cyclohexane quenches the triplet of acetone with a rate constant of $k_q = 3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.³³ This leads to a reduction in the triplet lifetime of acetone in cyclohexane to $\tau \leq 0.36 \mu\text{s}$; assuming this lifetime, a rate constant for the quenching of the acetone triplet by **2** of $9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and the concentration of **2** ($3 \times 10^{-4} \text{ M}$), the quantum yield for triplet quenching of acetone by **2** is approximately 0.49. Despite this reduced quenching efficiency, a significant contribution of the triplet state should have been detected.

Absolute quantum yields of acid generation were not determined, mainly because the value of the actinometer (triazine **2**) in cyclohexane was not available. However, in an experiment using the dye technique, the ratio of the acid production from **3** and **2** was determined to be 1:0.29. If the quantum yield of **3** was not affected by the solvent, that would translate into a quantum yield of photoacid generation of 0.11, a much higher value than that obtained in acetonitrile upon direct excitation.

Conclusion

Direct laser excitation of triazine **2** in acetonitrile leads to exclusive formation of the cation of 2^+ (see Schemes 2 and 3). Several isomeric structures have been proposed for this cation to account for its spectral and lifetime characteristics, with 7^+ being favored as the observable species. The quantum yield of heterolytic cleavage can be increased by roughly 1 order of magnitude by energy transfer from appropriate sensitizers; i.e., the triplet state reaction is more efficient than the reaction from the S_1 state, if the S_1 state contributes at all. With acetone and ITX, only energy transfer is observed; electron transfer does not play a role in the sensitization mechanism. Acid generation occurs via addition of 2^+ to a nucleophile with an dissociable hydrogen and subsequent release of a proton, probably followed by the cascade of events of Scheme 3.

In nonpolar solvents such as cyclohexane or benzene, the primary photochemical step in the photolysis of **2** is the homolytic cleavage of one of the carbon–chlorine bonds, yielding a radical pair; no subsequent electron transfer to the

(24) Appleton, D. C.; Brocklehurst, B.; McKenna, J.; McKenna, J. M.; Thackeray, S.; Walley, A. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 77.

(25) Cristol, S. J.; Greenwald, B. E. *Tetrahedron Lett.* **1976**, 2105.

(26) Cristol, S. J.; Bindel, T. H. *J. Am. Chem. Soc.* **1981**, 103, 7287.

(27) Cristol, S. J.; Bindel, T. H. *Org. Photochem.* **1983**, 6, 327.

(28) Slocum, G. H.; Schuster, G. B. *J. Org. Chem.* **1984**, 49, 2177.

(29) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, 85, 915.

(30) Chateaufneuf, J.; Luszyk, J.; Ingold, K. U. *J. Org. Chem.* **1988**, 53, 1629.

(31) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

(32) Watkins, A. R. *Chem. Phys. Lett.* **1980**, 70, 262.

(33) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin Cummings: Menlo Park, CA, 1978.

ion pair is observed. The highly reactive chlorine atom formed in this reaction abstracts a hydrogen atom to form hydrogen chloride. Contrary to the ionic pathway, population of the triplet state in nonpolar solvents has little influence on the amount of photogenerated acid.

Acknowledgment. This paper is dedicated to Dr. Keith U. Ingold, a good friend, an outstanding scientist, and a role model,

as he reaches a new milestone. Thanks are due to the Natural Sciences and Engineering Research Council (Canada) for support through its Strategic Grants Program. We are grateful to Professors F. L. Cozens and R. A. McClelland for reading a preliminary version of this paper.

JA983371C