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Laser Flash Photolysis Study of Two Aromatic *N*-Oxyimidosulfonate Photoacid Generators

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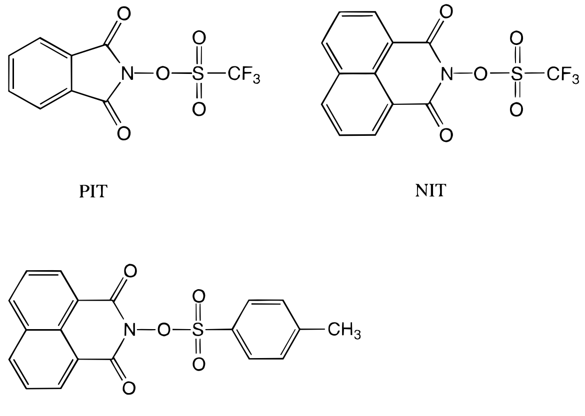
In this paper we study the photophysical and photochemical behavior of two aromatic *N*-oxyimidosulfonate photoacid generators (PAGs), *N*-trifluoromethylsulfonyloxy-phthalimide (PIT) and *N*-trifluoromethylsulfonyloxy-1,8-naphthalimide (NIT), by means of absorption and emission stationary techniques and nanosecond and picosecond laser flash photolysis. Triplet states have been detected for both compounds; lifetimes of 12 μs and 43 μs (acetonitrile solution) and 2 μs and 28 μs, (benzene solution), were measured for PIT and NIT, respectively. Photoacid generation quantum yields have also been measured ($\Phi = 0.28$ in acetonitrile, $\Phi = 0.21$ in benzene for PIT; $\Phi = 0.17$ in acetonitrile, $\Phi = 0.09$ in benzene for NIT), using Rhodamine B Base as an acid sensor and 2-methyl-4,6-bis(trichloromethyl)-1,3,5-triazine as a suitable actinometer with 308-nm laser excitation. Evidence that photoacid generation occurs through an ionic mechanism from the singlet state was obtained.

Introduction

During the past few years the field of microelectronics has been oriented toward the creation of new devices, characterized by an increasingly small size and high information content (from 64 MB DRAM, 0.35 μm feature, up to 1 GB DRAM, 0.18 μm, and 16 GB DRAM, 0.1 μm).[1] The bulk of the research has been in two different directions: the increase of achievable resolution and the creation of higher photosensitivity resists.[1,2] The first of these two objectives had been reached by using shorter wavelength radiations,[3−5] from visible to deep UV light, but only in recent years, by means of the substitution of the ordinary irradiation sources with excimer lasers,[6,7] was mass production achieved. The second purpose, that is, the design of higher sensitivity resists, has become possible by the use of specific molecules that improve the quantum efficiency of the process. Chemical amplification, as it has been termed, works through the photoproduction of a catalyst, usually from a photoacid generator (PAG).[8] A study of PAGs in solution is the first step to understand the photochemical behavior of these molecules; the results may then be used to predict their photochemistry in rigid media, such as polymers, which are closer to the systems currently employed in microlithographic processes.

Chart 1



PIT

NIT

NITos

In this work we studied the photochemical and photophysical behavior of two *N*-oxyimidosulfonate photoacid generators, *N*-trifluoromethylsulfonyloxy-phthalimide (PIT) and *N*-trifluoromethylsulfonyloxy-1,8-naphthalimide (NIT), with the aim to understand the mechanisms and efficiencies of photoacid generation. For the purpose of comparison, *N*-tosyloxy-1,8-naphthalimide (NITos) was also studied. The structures of these three molecules are shown in Chart 1.

The photochemistry of aromatic imides is known to be different from that of the other imides.[9] The Norrish type I cleavage is expected to be less efficient for these molecules than for the cyclic aliphatic imides, and thus, an increase of acid generation efficiency may be anticipated, since Norrish I cleavage may be a side reaction competing with the photoacid generation process. Upon UV excitation, *N*-oxyimidosulfonates probably exhibit

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N−O cleavage and subsequent formation of the sulfonic acid.[1,10] Some authors[11] have recently proposed a mechanism of reaction for a variety of sulfonate PAGs, that involves hydrogen abstraction from the solvent by the nitrogen position; however the mechanism has not been confirmed by laser flash photolysis. In the decomposition reaction of *N*-tosyloxy-phthalimide to form alkylamines, Cadogan and Rowley[12] proposed a mechanism involving a nitrogen-centered radical, while in related studies the reaction of *N*-tosyloxindole was suggested to proceed through either radical species[13] or a nitrenium ion[14] intermediate.

To measure the activity of PIT and NIT as PAGs, their photoacid generation quantum yields have been determined, using Rhodamine B base as acid sensor and 2-methyl-4,6-bis(trichloromethyl)-1,3,5-triazine (MTT) as an actinometer, according to a method established in previous work by Pohlers et al.[15] Evidence that the photoacid generation occurs through an ionic mechanism from the singlet state was obtained.

Experimental Section

Materials. The two PAGs were provided by Shipley Co. and recrystallized three times from hexanes (PIT) and chloroform (NIT). For the purpose of comparison, *N*-tosyloxy-1,8-naphthalimide (NITox) was also provided by Shipley Co. and used after recrystallization from chloroform. 2-Methyl-4,6-bis-(trichloromethyl)-1,3,5-triazine (MTT) was purchased from Panchim and purified by recrystallization from methanol (two times) and subsequent sublimation.

Rhodamine B base was obtained from Aldrich and purified by column chromatography on silica gel (230−400 mesh) using acetone as eluent. The purity of the dye was then checked by means of fluorescence excitation spectroscopy.

1,3-Cyclohexadiene was purchased from Aldrich and distilled before use. Anthracene (zone-refined, 99+%) was obtained from Aldrich and used as received; benzhydrol was purchased from Aldrich, recrystallized from hexane and then sublimed; tetrabutylammonium chloride was purchased from Fluka (>99%) and used without any further purification. Quinine sulfate dihydrate (99+%) was obtained from Acros and used as received.

Acetonitrile, benzene, methanol, tetrahydrofuran, and 2-methoxyethyl ether (diglyme) were all OmniSolv grade solvents from BDH and used as received.

General Techniques. Ground-state absorption spectra were recorded using a Varian Cary 1E spectrophotometer. Fluorescence spectroscopy was carried out on a Photon Technology International Version 1.2 X luminescence spectrometer. Suprasil quartz cells with a 10 mm optical path were employed in all these experiments.

For the nanosecond laser flash photolysis, a Lumonics EX-530 excimer laser (Xe/HCl, 308 nm, ~6 ns pulse width, 50−100 mJ/pulse) was used for excitation. The system is controlled by a Power Macintosh computer running LabVIEW 3.1.1 software (National Instruments). A Tektronix 2440 digital oscilloscope is used to digitize the signal from the photomultiplier tube. Further details on a similar laser system have been provided elsewhere.[16,17]

Fluorescence lifetimes were determined at 90° excitation with the third (355 nm) or the fourth harmonic (266 nm) of a pulsed-picosecond Nd:YAG laser and detection of the fluorescence using a Hamamatsu C-4334 Streak Camera. Further details have been provided elsewhere.[18]

Measurement Conditions. The optical densities of the samples used in the laser experiments were always kept in the 0.2−0.3 range. In the photoacid generation quantum yield measurements, optical density values were carefully matched to have differences in absorbance within 0.005. For transient absorption spectra a flow system (a 7 × 7 mm Suprasil quartz flow cell, connected with a 100 mL reservoir by means of Teflon tubing) was used. The flow technique was employed to allow irradiation of a fresh portion of the sample by each laser shot, thereby avoiding accumulation of photoproducts. However, when only a few laser shots were necessary, for example when recording kinetic decays or for quenching measurements, a static set up (7 × 7 mm Suprasil quartz cells) was used. This setup tends to provide longer lifetime values than those recorded by means of the flow system, because of the more efficient N_2 saturation of samples.

In the photoacid generation quantum yield experiments, because of the strong absorption of both the photoproducts formed upon photolysis of PAGs, and the indicator dye, a 500-mL reservoir was used in the flow system, along with a higher flow rate. Diglyme, which had been used to ensure the quantitative trapping of the chlorine atoms generated by photolysis of triazines, in the work by Pohlers et al.,[15] has been added to all acetonitrile and benzene solutions of PIT, NIT, and MTT (actinometer) in the photoacid generation quantum yield experiments in order to provide the standard, PIT and NIT samples with the same hydrogen donating medium.

To measure emission quantum yields, corrected areas of the samples and the standard (quinine sulfate dihydrate, dissolved in H_2SO_4 1 N, $\Phi_F = 0.546$[19]) were compared and corrected for the refractive index of the medium.

Results

Absorption Spectra. The absorption spectrum of PIT in acetonitrile solution consists of two distinct absorption bands: the first, very intense, at 219 nm (log $\epsilon = 4.7$); the second, much weaker, at 296 nm (log $\epsilon = 3.2$). In benzene solution, due to intense absorption by the solvent, only the longer wavelength band could be observed (297 nm, log $\epsilon = 3.2$).

The absorption spectrum of NIT exhibits a red shift, with respect to PIT, of the longer wavelength band, due to the presence of the naphthalene chromophore. In acetonitrile solution NIT shows two peaks, centered at $\lambda = 228$ nm (log $\epsilon = 4.6$) and $\lambda = 335$ nm (log $\epsilon = 4.2$). In benzene, the maximum of the longer wavelength absorption is observed at the same wavelength ($\lambda = 335$ nm, log $\epsilon = 4.1$).

Fluorescence Experiments. Fluorescence emission spectra of PIT and NIT, excited by 308-nm radiation in acetonitrile solution, show very different features. PIT emission is very weak, centered at about 360 nm, while the NIT spectrum is characterized by a more intense, structured band, whose maxima are found at 363 nm, 382 nm and ~400 nm (shoulder). Emission quantum yield values, measured using quinine sulfate dihydrate, dissolved in H_2SO_4 (1 N) as a standard, differ by 2 orders of magnitude: the quantum yield measured for NIT is

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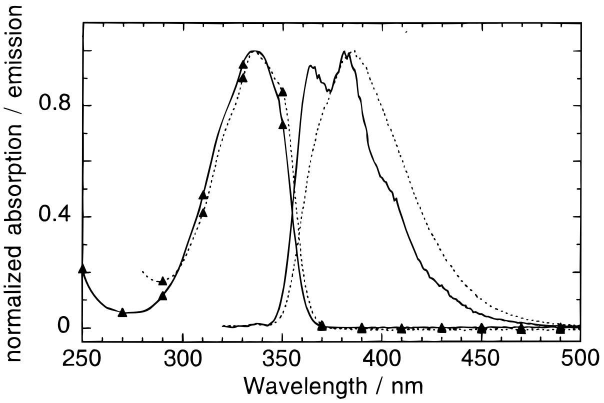

Figure 1. Ground-state absorption (▲) and fluorescence emission (no symbol) spectra of NIT in acetonitrile (—) and benzene (···) solutions.

Table 1. Singlet Lifetimes Measured by Picosecond Laser Flash Photolysis and Quantum Yield Values for Fluorescence Emission, Measured for PIT and NIT

	acetonitrile		benzene	
	Φ_F	τ_F(ns)	Φ_F	τ_F(ns)
PIT	10^{-3}	not measurable	6×10^{-3}	not measurable
NIT	0.12	0.48	0.39	1.95

0.12, the value for PIT is $\sim10^{-3}$. In benzene solution PIT still exhibits a very weak and noisy emission, while NIT is characterized by a strong emission band, centered at 386 nm, although its structure is less defined than in the acetonitrile spectrum. The emission quantum yields, measured in benzene solution, are 0.39 for NIT and 6×10^{-3} for PIT. The emission spectra of NIT in acetonitrile and benzene solution are shown in Figure 1, along with the corresponding absorption spectra.

Fluorescence lifetimes further demonstrate the difference betweeen the naphthyl and phenyl chromophores. Lifetimes of 480 ps and 1.95 ns were measured for NIT in acetonitrile and benzene solution, respectively, while for PIT it was impossible to evaluate its lifetime, due to the weakness of its emission intensity. The fluorescence parameters measured for PIT and NIT are summarized in Table 1.

Laser Flash Photolysis Measurements. *Transient Absorption Spectra and Kinetics.* The transient absorption spectrum obtained upon nanosecond laser flash photolysis (λ = 308 nm) of PIT in N_2-saturated acetonitrile solution, exhibits only one intense peak, with a maximum at 330 nm (Figure 2). The kinetic decay of this band (Figure 2, inset) follows first-order kinetics, with a lifetime of 12 μs. The transient absorption spectrum of PIT in N_2-saturated benzene solution does not show any appreciable difference with respect to that recorded in acetonitrile; however, the transient lifetime is shorter (2 μs).

In contrast, NIT transient absorption spectrum, recorded in N_2-saturated acetonitrile solution, is characterized by a broad structured band, with two peaks centered at 370 and 470 nm and a sharp bleaching region between 310 and 360 nm (Figure 3). This negative signal, centered at 340 nm, does not recover completely and it is stable over a 20-ms time window. The kinetic decays, monitored at 370 and 470 nm, are described well by a first-order fit, giving a lifetime of 43 μs. The kinetic trace recorded at 470 nm, is shown in the inset of Figure 3. Much of the behavior in N_2-saturated benzene solution is quite similar, with the NIT transient still exhibiting two distinct absorption maxima at 370 and 470 nm (Figure 4), whose lifetime, obtained by means of a first-order fit, is 28 μs (Figure 4, inset). The main difference is represented by the

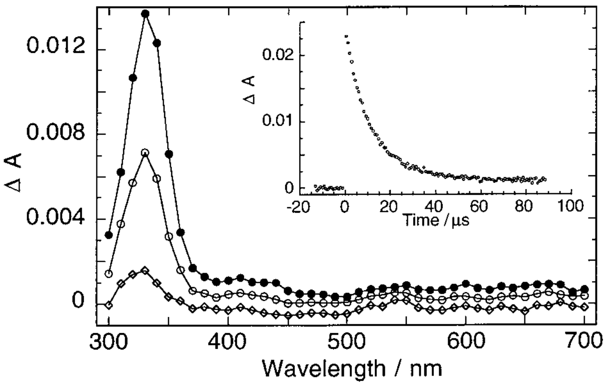

Figure 2. Transient absorption spectra obtained upon nanosecond laser flash photolysis of PIT in N_2-saturated acetonitrile solution: (●) 0.7 μs; (○) 2.6 μs, and (◇) 6.6 μs after the laser pulse. Inset: decay kinetic monitored at 330 nm, recorded using a static setup.

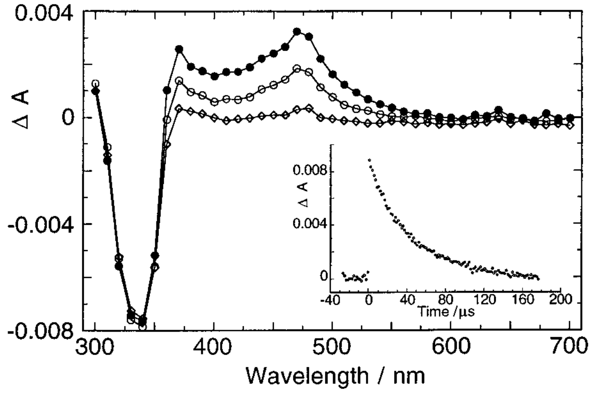

Figure 3. Transient absorption spectra obtained upon nanosecond laser flash photolysis of NIT in N_2-saturated acetonitrile solution: (●) 1 μs; (○) 3.4 μs, and (◇) 8.3 μs after the laser pulse. Inset: Decay kinetic monitored at 470 nm, recorded using a static setup.

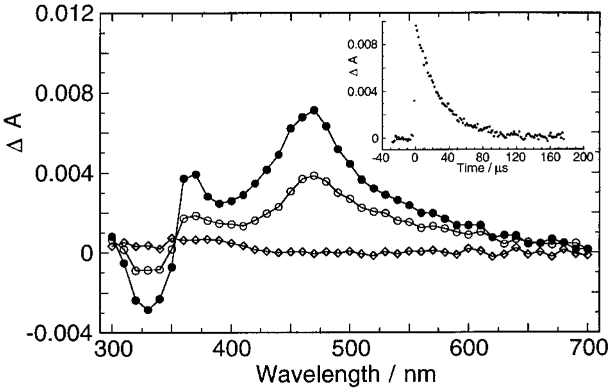

Figure 4. Transient absorption spectra obtained upon nanosecond laser flash photolysis of NIT in N_2-saturated benzene solution: (●) 0.7 μs; (○) 2.4 μs, and (◇) 16 μs after the laser pulse. Inset: Decay kinetic monitored at 470 nm, recorded using a static setup.

Table 2. Spectral and Kinetic Parameters of PIT and NIT, Measured by Nanosecond Laser Flash Photolysis

	acetonitrile		benzene	
	λ_{max} (nm)	τ (μs)	λ_{max} (nm)	τ (μs)
PIT	330	12	330	2
NIT	370, 470	43	370, 470	28
	340 (bleaching)	stable	330 (bleaching)	

bleaching region (310−360 nm); in benzene solution the negative signal at 330 nm undergoes complete recovery within the same lifetime of the main transient decay. A residual absorption area, although very weak in intensity (ΔA < 0.001), is observed in the spectral range between 330 and 420 nm.

The spectral and kinetic parameters obtained upon laser flash photolysis are summarized in Table 2.

Quenching Experiments. To characterize the nature of the transient observed upon nanosecond laser flash photolysis, a series of experiments with various quencher species were performed. The transient observed upon PIT photolysis in acetonitrile is quenched by oxygen with a rate costant $k = 4.2 \times 10^8$ M^{-1} s^{-1}; the corresponding value obtained in benzene solution is not significantly different, $k = 3.1 \times 10^8$ M^{-1} s^{-1}. The NIT transient is quenched by oxygen with a rate constant $k = 6.5 \times 10^8$ M^{-1} s^{-1} in acetonitrile solution and $k = 6 \times 10^8$ M^{-1} s^{-1} in benzene. Both lifetimes and ΔA of the long-lived negative signal, observed at 340 nm in the photolysis of NIT in acetonitrile, are not influenced by the presence of oxygen.

The effects of tetrabutylammonium chloride, an ion-pair reagent with a strong nucleophilic activity due to Cl$^-$ anions, were studied up to a concentration of 2×10^{-3} M; this quencher does not affect the kinetic behavior of PIT and NIT transients, observed respectively at 330 and 470 nm. However, when a concentration of 2×10^{-3} M was added to a NIT solution in acetonitrile, a decrease of more than a half of the ΔA of the bleaching signal recorded at 340 nm was observed, although its lifetime was not affected by the quencher. The same ΔA decrease was found upon addition of 0.24 M methanol to NIT acetonitrile solution.

Benzhydrol, whose activity as a photoreducing agent involves hydrogen atom donation[20,21] to form the corresponding diphenylketyl radical[22] is well-known, was added to solutions up to a concentration of 2×10^{-3} M, but no effect on the aforementioned species was detected.

Another quencher, 1,3-cyclohexadiene, has also been used due to its relatively low triplet energy (219 kJ mol^{-1})[23] and its diffusion-controlled quenching activity toward triplet states of different molecules in various solvents.[24] 1,3-Cyclohexadiene efficiently quenches both PIT and NIT transients, giving rate constants of 7.9×10^9 and 5.0×10^9 M^{-1} s^{-1}, respectively, in acetonitrile solution.

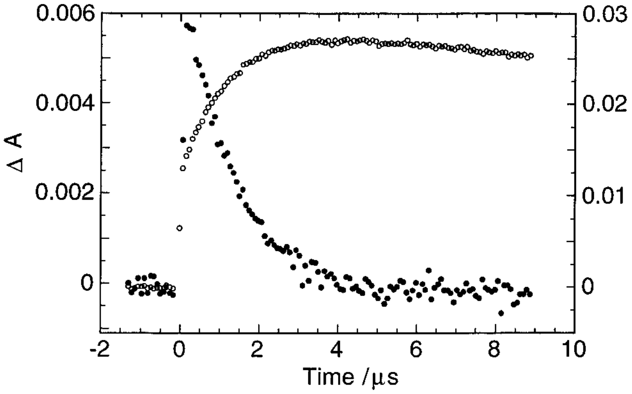

Figure 5. Kinetic traces recorded upon laser flash photolysis of PIT in the presence of 4.5×10^{-5} M anthracene in N$_2$-saturated benzene solution; monitored at 340 nm (●) and 430 nm (○).

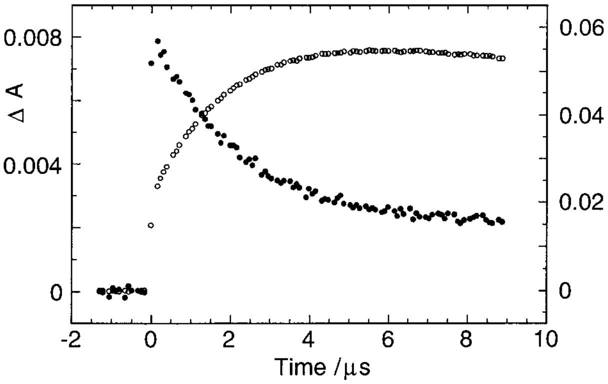

Figure 6. Kinetic traces recorded upon laser flash photolysis of NIT in the presence of 6.7×10^{-5} M anthracene in N$_2$-saturated benzene solution; monitored at 470 nm (●) and 430 nm (○).

Anthracene (energy of lowest triplet state: 177 kJ mol^{-1})[23] was also used as a triplet quencher and efficiently quenched both PIT and NIT transients with rate constants of 7.3×10^9 and 5.7×10^9 M^{-1} s^{-1}, respectively. In both cases, the decrease of transient lifetime upon increasing anthracene concentration, was accompanied by a first-order growth monitored at 430 nm (Figures 5 and 6, respectively), a wavelength which is characteristic of anthracene triplet absorption in benzene solution.[25]

The rate constants, describing the reactivity of the transients observed upon nanosecond laser flash photolysis of PIT and NIT toward different quenchers, are shown in Table 3.

Photoacid Generation Quantum Yields. The photoacid generation quantum yields were measured by means of the nanosecond laser flash photolysis apparatus. Upon laser excitation of PAGs, acid species are produced in solution and their presence is detected by the protonation of Rhodamine B, whose characteristic signal is monitored at 550 nm. For each sample, that is, MTT, PIT, and NIT, the maximum ΔA observed at 550 nm was plotted as a function of laser energy. The slopes of linear plots, obtained according to this procedure (Figure 7), were used to evaluate the photoacid generation

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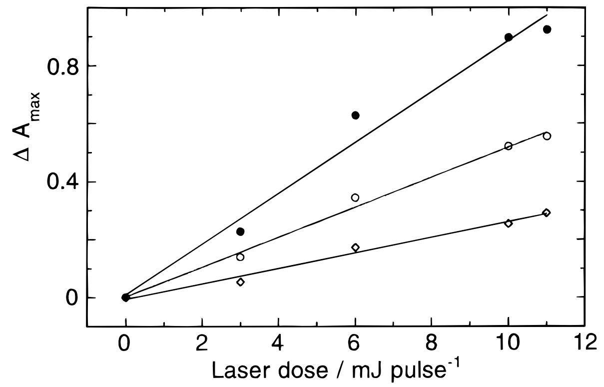

Figure 7. Maximum ΔA values due to rhodamine B cation, observed at 550 nm, upon laser excitation of MTT (●), PIT (○), and NIT (◇) in N_2-saturated acetonitrile solution, as a function of laser dose.

Table 3. Effect of Different Quenchers on the Kinetic Decay of Transients Observed upon Nanosecond Laser Flash Photolysis of PIT and NIT

	k_q (M^{-1} s^{-1})	
quencher	PIT (monitored at 330 nm)	NIT (monitored at 470 nm)
O_2 (acetonitrile)	4.2×10^8	6.5×10^8
O_2 (benzene)	3.1×10^8	6.0×10^8
1,3-cyclohexadiene	7.9×10^9	5.0×10^9
anthracene	7.3×10^9	5.7×10^9
benzhydrol	no effect up to 2×10^{-3} M	no effect up to 2×10^{-3} M
tetrabutylammonium chloride	no effect up to 2×10^{-3} M	no effect up to 2×10^{-3} M

Table 4. Photoacid Generation Quantum Yield Values, Measured for PIT and NIT, Compared with Corresponding Values Obtained for Fluorescence Quantum Yields

	acetonitrile		benzene	
	Φ_{PAG}	Φ_F	Φ_{PAG}	Φ_F
PIT	0.28	10^{-3}	0.21	6×10^{-3}
NIT	0.17	0.12	0.089	0.39

quantum yields. By introducing the slope values in the following simple expression:

$$\Phi_{PAG} = \Phi_{STD} \times \frac{\text{slope}_{PAG}}{\text{slope}_{STD}}$$

where $\Phi_{STD} = 0.45$[26] is the photoacid generation quantum yield for the actinometer, the photoacid generation quantum yields of PIT and NIT have been obtained. The Φ_{PAG} values measured for the two molecules in acetonitrile and benzene solution are shown in Table 4.

It is important to note that although these measurements were carried out in the presence of 0.5 M diglyme, as described in the Experimental Section, the photoacid generation quantum yield values were found to be the same even in the absence of diglyme.

Moreover, the presence of 4×10^{-3} M benzhydrol did not produce any effect on the photoacid generation process for both PIT and NIT. In contrast, when 2×10^{-3} M tetrabutylammonium chloride was added to PAG solutions, the photoacid generation quantum yields were significantly lower: a reduction of 2 times and 6 times were observed for PIT and NIT, respectively.

Discussion

The transient absorption spectra of PIT and NIT in acetonitrile and benzene solutions show the presence of just one intermediate in the photolysis process; however, in the case of NIT, a residual negative (bleaching) absorption was also observed in acetonitrile solution, in the 310−360-nm range, indicating the formation of a stable product.

The spectral shape of PIT and NIT transients is essentially the same in both acetonitrile and benzene; this is an indication that the species observed is the same in both solvents. The absence of any effect on transient decay upon addition of an ionic quencher (tetrabutylammonium chloride) to the solution suggests that the intermediate is not an ionic one.

The kinetics are also unaffected by the presence of benzhydrol, but are markedly affected by 1,3-cyclohexadiene. In light of the fact that benzhydrol can act as a radical quencher by hydrogen donation and 1,3-cyclohexadiene can behave as both radical and triplet quencher, we can assign the identity of the transient as the triplet state. To confirm our assignment of the transients to the triplet states of PIT and NIT, we decided to analyze the effect of anthracene, which has a triplet energy lower than that of 1,3-cyclohexadiene and cannot act as radical scavenger, on the kinetic decay of PAG-derived transients. The quenching effect of anthracene was notable (7.3×10^9 and 5.7×10^9 M^{-1} s^{-1} for PIT and NIT, respectively) and the presence of the kinetic growth of the anthracene triplet (430 nm), whose rise time matches the kinetic decay of PIT transient (340 nm) and NIT transient (470 nm) in the respective experiments in benzene solution, confirms that anthracene triplet sensitization has occurred via the PAG triplet state.

The assignment of the transients observed upon photolysis experiments to the triplet state of the photoacid generators is also reasonable if we consider the absorption maximum values reported in the literature for benzene (235 nm in nonaromatic solvents)[25] and naphthalene (415 nm[25] and 425[27] in benzene, 415 nm in nonaromatic medium[25,27]) triplet states, and the presumable red shift that PIT and NIT triplets would undergo with respect to them, due to the conjugation of the aromatic rings with the CO−N−CO system.

The oxygen quenching values may seem low given that the transients are triplet state species. However, rate constants lower than 10^9 M^{-1} s^{-1} have been reported in the literature for oxygen quenching of highly conjugated aromatic systems such as coronene (0.42×10^8 M^{-1} s^{-1} in benzene solution[28]) and 1,3,5-triphenylene (0.7×10^8 M^{-1} s^{-1} in hexane[29]).

Moreover, the triplet state is the only transient species we observe either in PIT or NIT photolysis, since there is no evidence of other species forming with a rise time which matches the triplet state decay. In addition, the triplet states observed are rather long-lived to be

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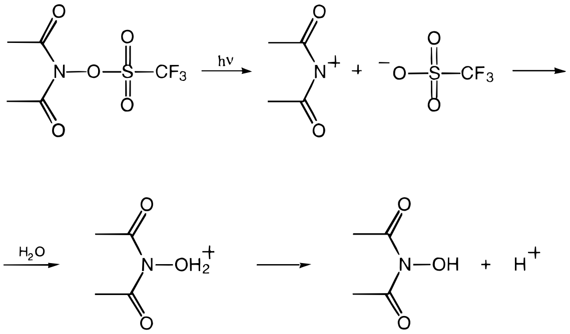
precursors of other species. Even the stable negative signal observed upon NIT photolysis in acetonitrile in the 310−360 nm range, does not show any growth in the shortest time scale we could use in the nanosecond laser experiments; that is, it is formed within the laser pulse and the triplet state is not its precursor. This last conclusion is also supported by the experiments with tetrabutylammonium chloride, which only affects the photoacid generation quantum yields but not triplet decay.

The photoacid generation experiments clearly show that PIT, and to a lesser extent NIT, produce acid species upon photolysis. We suggest that the excited-state involved in the photoacid generation process is the singlet state of the PAGs. If this is the case, processes such as fluorescence emission and photoacid generation would be in competition in the deactivation of singlet state of PAGs. If we take into account all the data collected in Tables 1 and 4, it can be seen that PIT is the molecule characterized by the highest values for photoacid generation quantum yields, but it also shows very weak emissions in both acetonitrile and benzene solutions. In contrast, NIT exhibits higher values for fluorescence quantum yields, along with lower quantum yields for photoacid generation. Furthermore, going from acetonitrile to benzene, NIT emission quantum yield increases from 0.12 to 0.39 and the corresponding fluorescence lifetime changes from 480 ps to 1.95 ns, while photoacid generation quantum yield decreases from 0.17 to 0.089. All these facts support the idea that the photoacid generation process is in competition with emission in the deactivation of singlet excited-state PAGs.

It is now important to establish which is the mechanism of reaction that leads to acid production and which is the nature of the species involved. An important result is that photoacid generation quantum yields, in both acetonitrile and benzene solutions, are not affected by the presence of a radical quencher (see diglyme and benzhydrol experiments), but they are reduced when an ionic quencher is added to the solution (e.g., tetrabutylammonium chloride). This is a clear indication that the process leading to the final products of photolysis involves ionic intermediates. One of the final products is detectable in the laser flash photolysis of NIT in acetonitrile, as the stable negative signal in the spectral region between 310 and 360 nm indicates. As we have already seen, this product is immediately formed from the singlet state of NIT and its accumulation does not allow the signal in the “bleaching region” to recover completely. In the mass spectrum recorded on the final products, obtained by evaporating the solvent from the photolyzed acetonitrile solution of NIT, the presence of *N*-hydroxy-naphthalimide has been detected; moreover, the ground state absorption spectrum, recorded on a known sample of *N*-hydroxy-naphthalimide, confirms that the absorption of this molecule approximately extends between 300 and 360 nm. Therefore, we may suggest that upon photolysis of NIT, heterolytic cleavage of the N−O bond (GS-MS experiments on PIT and NIT also suggest that the N−O bond is the weakest in these PAG molecules) occurs, with subsequent formation of ionic intermediates and production of *N*-hydroxy-naphthalimide after reaction with water, as shown in Scheme 1. The heterolytic cleavage is probably favored over homolytic cleavage because the triflate anion is an excellent leaving group. In fact, the strong electron-withdrawing effect on the oxygen atom, due to the presence of three fluorine atoms in the sulfonate moiety of the PAG, makes the triflate anion one of the best leaving groups in a relative ability scale of sulfonate groups.[30] Scheme 1 requires the presence of water to observe photoacid generation. This is not unlikely, since we note that even in high-grade acetonitrile, a significant amount of water is present: in our photolysis experiment, the concentration of water (0.003 wt % according to the manufacturer) was 1.3×10^{-3} M, that is at least 1 order of magnitude higher than the PAG concentration. Further, the experiments with nucleophilic species, like chloride anions (from tetrabutylammonium chloride) and methanol, caused a reduction in the bleaching ΔA at 340 nm, due to competition with water on adding to the $CO{-}N^{+}{-}CO$ site. This fact causes a consequent decrease of photoacid generation quantum yield and a diminution of *N*-hydroxynaphthalimide formation. Finally, our hypothesis of a heterolytic cleavage of the N−O bond with subsequent formation of an electrophilic N^{+} site, has been further confirmed by a photolysis experiment in methanol. The analysis of the crude photolyzed products, by means of a mass spectrum, showed the presence of *N*-methoxynaphthalimide, indicating a nucleophilic attack at the nitrogen position.

Scheme 1



The mechanism we have proposed can also be extended to NIT in benzene and PIT in both acetonitrile and benzene solutions since the results we obtained suggest that, even in benzene, photoacid generation follows the same reaction pathway. Although benzene has a lower polarity than acetonitrile, its typical water content is even higher (5×10^{-3} M). The experimental result that photoacid generation quantum yields are not affected by benzhydrol and diglyme, but undergo a reduction when tetrabutylammonium chloride is added indicate that the process still involves the same mechanism as in acetonitrile. The lower quantum yields of photoacid generation observed in benzene, with respect to the acetonitrile solution, may be explained considering the fact that forming ionic species is energetically less feasible in a solvent with a low dieletric constant such as benzene.

Mass spectra were also recorded before and after photolysis of NIT in benzene and PIT in both solvents;

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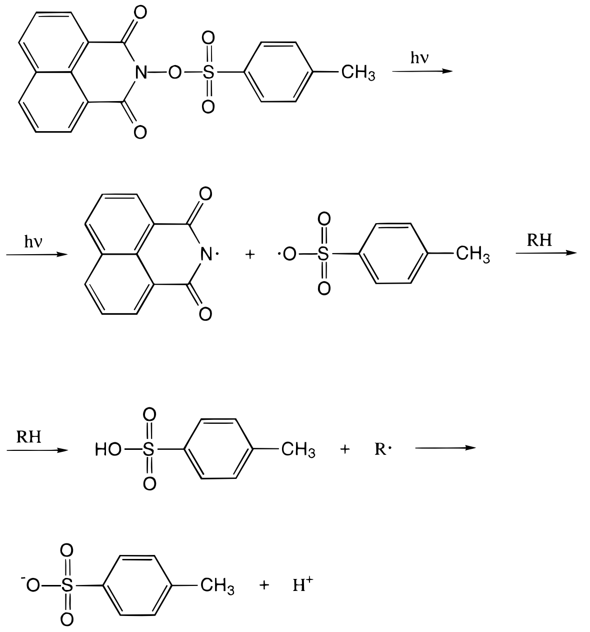
(30) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, *85*.

Scheme 2



in all cases the formation of the *N*-hydroxy derivative was found, confirming our hypothesis. The absence of the persistent negative signal in the photolysis of NIT in benzene, where the signal at 340 nm exhibits a complete recovery, may be explained by taking into account the lower quantum yield for photoacid generation in benzene with respect to acetonitrile and in terms of different extinction coefficients for *N*-hydroxy-naphthalimide in acetonitrile and benzene. In the photolysis of PIT, the bleaching signal was not observed in the range 300−700 nm, due to the blue-shifted absorption of the product (*N*-hydroxy-phthalimide) with respect to *N*-hydroxy-naphthalimide.

The formation of the highly stable trifate anion is therefore the driving force for the heterolytic cleavage in the photolysis of PIT and NIT. Further support for the important role played by the triflate anion is given by some photolysis experiments that we performed on another photoacid generator of analogous structure, but not containing the triflic group: the *N*-tosyloxy-1,8-naphthalimide. The photoacid generation quantum yield of this PAG has been measured in benzene ($\Phi = 0.027$), where the mechanism is more likely to occur through a homolytic cleavage of the N−O bond. In fact, a radical reaction pathway in the 254-nm photolysis of a molecule of similar structure, *N*-tosyloxy-phthalimide, was already proposed by some authors.[31] We found that the quantum yield for photoacid generation of NITos is strongly influenced by the presence of hydrogen donors, such as tetrahydrofuran and diglyme, but it is not affected by the presence of tetrabutylammonium chloride, a nucleophilic quencher. This is in stark contrast to what we observed in the corresponding experiments with PIT and NIT, where a nuclophilic quencher greatly reduced the photoacid generation quantum yields. This supports the homolytic nature of the photolysis reaction for PAGs whose “acid moiety” does not contain a very good leaving group such as the triflate anion. The reaction mechanism of *N*-tosyloxy-1,8-naphthalimide may therefore be drawn as shown in Scheme 2.

Conclusion

We can conclude that for the two PAG molecules we studied, *N*-trifluoromethylsulfonyloxy-phthalimide (PIT) and *N*-trifluoromethylsulfonyloxy-1,8-naphthalimide (NIT), photoacid generation constitutes one of the principal photoreaction pathways; this behavior may be related to the low reactivity of aromatic imides in other photochemical processes, such as Norrish I type C−CO bond cleavage.

Triplet states of the molecules are rather long-lived and are not involved in the mechanism of acid generation; a series of experimental results such as emission quantum yields, singlet-state lifetime measurements, photoacid generation quantum yields, and the presence of a stable species formed within the laser pulse in the photolysis experiments, indicates that photoacid generation occurs from the singlet excited state of these PAGs.

Photoreaction proceeds through heterolytic cleavage of the N−O bond with subsequent production of ionic intermediates, leading to acid generation and formation of the corresponding *N*-hydroxy-imido compound. This reaction pathway is possible because of the presence of the triflic group in the “acid moiety” of the PAGs, leading upon photolysis to the stable triflate anion. When this latter unit is replaced by the tosyl group, the mechanism of reaction changes, and photoacid generation occurs through homolytic cleavage of the N−O bond.

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[31] Brunsvold, W.; Kwong, R.; Montgomery, W.; Moreau, W.; Sachdev, H.; Welsh, K. Advances in Resist Technology and Processing VII. *SPIE* **1990**, *1262,* 162.