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Mechanism of Reaction and Photoacid Generation of *N*-Oxysuccinimidoarylsulfonate PAGs: A Laser Flash Photolytic Study

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The photochemical behavior of four *N*-oxysuccinimidoarylsulfonate photoacid generators (PAGs), 1-[[phenylsulfonyl]oxy]- (PSPD), 1-[[(4-methylphenyl)sulfonyl]oxy]- (MSPD), 1-[[(4-fluorophenyl)sulfonyl]oxy]- (FSPD), 1-[[(4-chlorophenyl)sulfonyl]oxy]-2,5-pyrrolidinedione (CSPD), has been studied by means of nanosecond laser flash photolysis ($\lambda_{exc} = 266$ nm) and steady-state photolysis ($\lambda_{exc} = 254$ nm) with the aim of understanding the reaction mechanism and, particularly, photoacid generation pathways and efficiency in the deep UV region. Upon photoexcitation, the formation of arylsulfonyl radicals and their subsequent desulfonylation were detected for the four PAGs. In oxygen-saturated solution, the generation of the corresponding arylperoxy radicals was also observed. Photoacid generation quantum yields upon laser excitation were found to range from 0.04 to 0.05. Product studies following steady-state irradiations reveal that acid generation is dominated by the formation of sulfonic acids.

Introduction

Photoacid generators (PAGs) are of primary importance in microlithography, particularly for applications in the microelectronics industry. In the production of positive tone resists, an acid is normally used to render the polymeric substrate more soluble in the developing solvent, whereas in the case of negative tone resists, the presence of an acid is required to catalyze polymeric cross-linking, thereby making the substrate more solvent-resistant during the developing step.[1−4] This “chemical amplification” is possible through the photogeneration of the acid species required, and for this purpose photoacid generators are commonly used in the microlithographic industry.[1,3] Therefore, the study of the possible reactions that these molecules can undergo upon photoexcitation is important to gauge their potential for use as PAGs in microlithographic applications.

Our work involves a group of *N*-oxysuccinimidoarylsulfonate potential PAGs, which we study by means of continuous irradiation and nanosecond laser flash photolysis techniques. The four PAGs under consideration here have the 1-[[(X)sulfonyl]oxy]-2,5-pyrrolidinedione structure, where the substituent X is −H (phenyl) (PSPD), $-CH_3$ (4-methylphenyl) (MSPD), −F (4-fluorophenyl) (FSPD), and −Cl (4-chlorophenyl) (CSPD).

Although we could not find any laser flash photolytic work on these specific molecules in the literature, it is well-known[5] that cyclic aliphatic imides can undergo cleavage reactions similar to the Norrish I photoreaction, occurring either on the C−CO or on the N−CO bonds. These reaction pathways can compete undesirably with photoacid generation. Our goal was to investigate the photochemistry of *N*-oxysuccinimidoarylsulfonate PAGs to understand the mechanism of reaction and photoacid generation of these species.

To aid in this understanding, the photoacid generation quantum yields (Φ_{acid}) of these PAGs under laser irradiation at 266 nm have been determined. Additionally, the quantum yield of decomposition of PAG (Φ_{decomp}), and the quantum yield of *p*-toluenesulfonic acid formation (Φ_{PTSOH}) for MSPD under steady-state irradiation at 254 nm have also been determined.

Experimental Section

Materials. The four photoacid generators (PSPD, MSPD, FSPD, and CSPD) were prepared by reaction of *N*-hydroxysuccinimide with the appropriate arylsulfonyl chloride in a manner similar to that described in the literature for analogous compounds.[6] Chemical purities were determined by HPLC; NMR spectra were measured at 400 MHz in $CDCl_3$.

PSPD: mp 108.6 °C; yield 95%; purity 99.9%; ^1H NMR δ 8.06 (m, 2H), 7.77 (m, 1H), 7.62 (m, 2H), 2.82 (s, 4H). **MSPD**:

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mp 145.1 °C; yield 90%; purity 100%; ^{1}H NMR δ 7.94 (d, 2H), 7.42 (d, 2H), 2.82 (s, 4H), 2.49 (s, 3H). **FSPD**: mp 112.4 °C; yield 85%; purity 100%; ^{1}H NMR δ 8.10 (m, 2H), 7.30 (m, 2H), 2.84 (s, 4H). **CSPD**: mp 169.3 °C; yield 85%; purity 99.5%; ^{1}H NMR δ 8.00 (d, 2H), 7.59 (d, 2H), 2.83 (s, 4H).

Anthracene (zone-refined, >99%), 3-chloro-2-chloromethyl-1-propene (>99%), *p*-methoxyphenol (99%), triethylamine (99%), 2,2,6,6-tetramethyl-1-piperidinyloxy, free radical (TEMPO, 99%), potassium iodide (99%), potassium iodate (99.5%), sodium tetraborate decahydrate (≥ 99.5%) and *p*-toluenesulfonic acid monohydrate (98.5%) were obtained from Aldrich and used as received. Benzhydrol (99%) was purchased from Aldrich, recrystallized from hexane, and then sublimed; tetrabutylammonium chloride was purchased from Fluka (>99%) and used without any further purification. 2,3-Dimethyl-1-butene (97%) was received from Aldrich and distilled before use. $CuCl_2$ (97%) was supplied by Aldrich and recrystallized twice from a dilute solution of hot HCl.

2-Methyl-4,6-bis(trichloromethyl)-1,3,5-triazine (MTT) was purchased from Panchim and purified by recrystallization from methanol (2 times) and subsequent sublimation. Benzophenone was supplied by BDH (99%) and recrystallized twice from ethanol/water before use. Rhodamine B base was obtained from Aldrich and purified by column chromatography on silica gel (230−400 mesh) using acetone as the eluent. The spectroscopic quality of the dye was then verified by means of fluorescence excitation spectroscopy.

Acetonitrile, tetrahydrofuran (THF), and 2-methoxyethyl ether (diglyme) were all OmniSolv-grade solvents from BDH and used as received. 2-Propanol, HPLC-grade from Sigma-Aldrich, was used as received.

General Techniques. Ground-state absorption spectra were recorded using a Varian Cary 1E spectrophotometer. Suprasil quartz cells with a 10-mm optical path were employed in these experiments.

For the nanosecond laser flash photolysis, the fourth harmonic ($\lambda_{exc} = 266$ nm) from a Surelite Nd:YAG laser (<10 ns pulse width, ~20 mJ/pulse) was used for excitation. The system was controlled by a Power Macintosh computer running LabVIEW 4.1 software (National Instruments). A Tektronix 2440 digital oscilloscope was used to digitize the signal from the photomultiplier tube. Suprasil quartz cells (7 × 7 mm) were used in these experiments. Further details of a similar laser system have been provided elsewhere.[7,8]

Steady-state irradiations were performed in a photoreactor equipped with RPR-2540 lamps ($\lambda_{exc} = 254$ nm) from the Southern New England Ultraviolet Co. Quartz cells of the same type as for laser flash photolysis experiments were used and rotated by means of a "merry-go-round" apparatus to ensure that all of the samples received the same irradiation dose.

Product studies on these steady-state irradiations were performed on a HPLC (Varian 9010 pump with a model 9065 autosampler and a model 9090 diode array detector interfaced to a 386 computer equipped with Star Workstation software) employing a 25-cm Zorbax C-18 column with a 25% water/75% methanol mobile phase. Products were further characterized by LC/MS analysis in a Millennium system using a reverse-phase column and a combination of UV diode array and mass spectroscopic detection.

Measurement Conditions. The absorbance values of the samples used in the laser experiments were 0.3−0.5 at the excitation wavelength. In the Φ_{acid} measurements under laser irradiation, absorbance values were carefully matched so that the differences in absorbance were less than 5×10^{-3}. For transient absorption spectra, a flow system (a 7 × 7 mm Suprasil quartz flow cell connected to a 100-mL reservoir by means of Teflon tubing) was used. The flow technique was employed to allow for irradiation of a fresh portion of the sample, thereby avoiding accumulation of photoproducts. However, when only a few laser shots were necessary, for example when recording kinetic decays or making quenching measurements, a static set up (7 × 7 mm Suprasil quartz cells) was preferred.

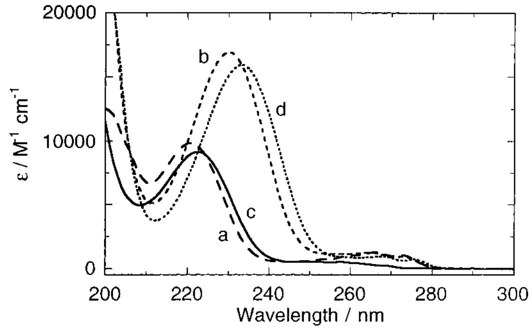

Figure 1. Ground-state absorption spectra of (a) PSPD, (b) MSPD, (c) FSPD, and (d) CSPD in acetonitrile solutions.

The Φ_{acid} experiments performed using laser irradiation are based on the protonation of rhodamine B base (Rb), whose characteristic signal following protonation is monitored at 550 nm. The details of this technique with MTT used as an actinometer at 308 nm are described elsewhere.[9,10] The quantum yield of MTT at 266 nm was determined in the present study using a calibration technique described elsewhere[11] that is based on quantitative trapping of the $Cl^{\bullet}$ radicals produced upon photolysis of MTT in the presence of Cl^- anions and subsequent detection of the $Cl_2^{\bullet -}$ complex ($\epsilon_{355} = 7100$ M^{-1} cm^{-1}).[12] Triplet benzophenone formation in acetonitrile was used as an actinometer for this calibration with 266-nm laser excitation ($\lambda_{max} = 520$ nm, $\epsilon_{520} = 6500$)[13] and a quantum yield of triplet formation of 1.0.[14] The value obtained for Φ_{acid} of MTT at 266 nm was 0.28.

In the quantum yield experiments performed under steady-state 254-nm conditions, diglyme (0.5 M) was added as a hydrogen-atom donor (for consistency with the MTT work). The actinometer consists of a solution of 0.5−0.6 M potassium iodide and 0.1 M iodate in 0.01 M borate buffer, which has a quantum yield of 0.75.[15] After irradiation, the formation of triiode is monitored at 472 nm ($\epsilon_{472} = 595$) in a spectrophotometer. The Φ_{acid} value for MSPD was determined using Rb, which was added to samples following irradiation, as an acid sensor. The Φ_{decomp} and Φ_{PTSOH} values were determined via HPLC analysis of these samples.

Results and Discussion

The absorption spectra (Figure 1) of the four PAGs in acetonitrile solution exhibit a main peak at 221 nm ($\log \epsilon = 4.0$) for PSPD, 230 nm ($\log \epsilon = 4.2$) for MSPD, 223 nm ($\log \epsilon = 4.0$) for FSPD, and 233 nm ($\log \epsilon = 4.2$) for CSPD; another weaker ($\log \epsilon \leq 3.3$) and broad band extends from 250 to 280 nm for all four molecules. Both 254- and 266-nm excitations, therefore, can be used to photolyze these molecules.

The transient absorption spectra obtained upon nanosecond laser flash photolysis ($\lambda = 266$ nm) of the four *N*-oxysuccinimidoarylsulfonate PAGs in N_2-saturated acetonitrile solution exhibit common features (Figures

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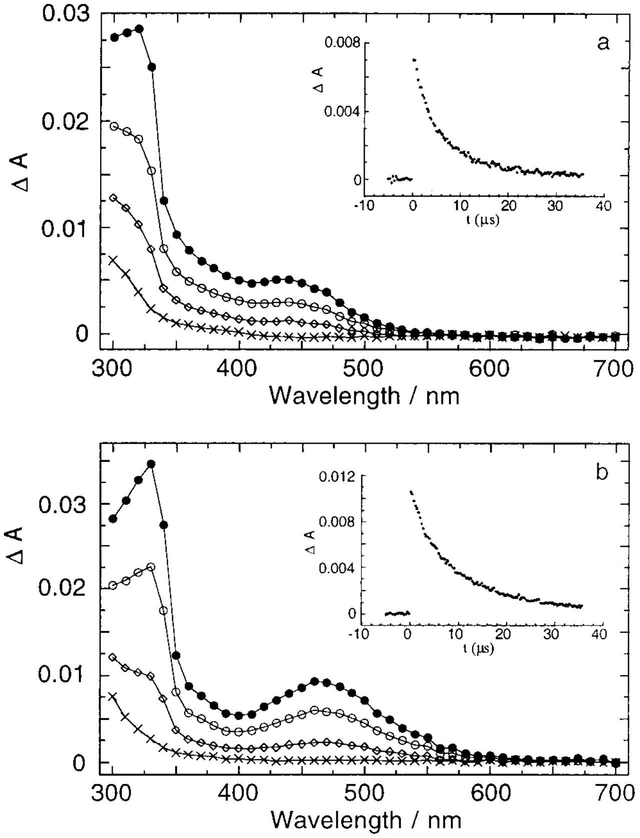

Figure 2. Transient absorption spectra obtained upon nanosecond laser flash photolysis of (a) PSPD and (b) MSPD in N_2-saturated acetonitrile solution. For part a, spectra recorded (●) 1.1, (○) 3.8, (◇) 9.3, and (×) 31 μs after the laser pulse. For part b, spectra recorded (●) 1, (○) 4, (◇) 13, and (×) 31 μs after the laser pulse. Insets: Decay kinetics monitored at (a) 430 and (b) 460 nm.

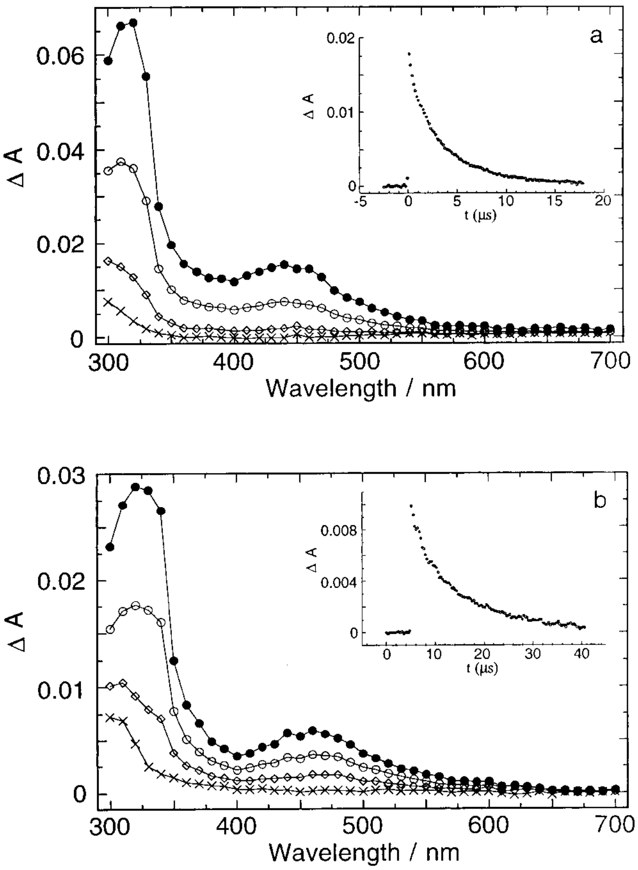

Figure 3. Transient absorption spectra obtained upon nanosecond laser flash photolysis of (a) FSPD and (b) CSPD in N_2-saturated acetonitrile solution. For part a, spectra recorded (●) 0.6, (○) 3.4, (◇) 12, and (×) 32 μs after the laser pulse. For part b, spectra recorded (●) 1.1, (○) 4.5, (◇) 12, and (×) 32 μs after the laser pulse. Insets: Decay kinetics monitored at (a) 440 and (b) 460 nm.

Table 1. Spectral and Kinetic Characteristics of the Transients Observed upon Laser Flash Photolysis in N_2-Saturated Acetonitrile Solution and Photoacid Generation Quantum Yields Measured for the Four *N*-Oxysuccinimidosulfonate PAGs

	λ (nm)	τ (μs)	Φ_{acid}
PSPD	320, 430	12.1	0.04
MSPD	330, 460	18.6	0.04
FSPD	320, 440	13.7	0.05
CSPD	320, 460	9.4	0.05

Table 2. Effects of Different Quenchers on Lifetimes of the Transients Observed upon Laser Flash Photolysis in N_2-Saturated Solution

	k_q (M^{-1} s^{-1})			
	PSPD	MSPD	FSPD	CSPD
oxygen	1.1×10^9	1.2×10^9	9.8×10^8	1.2×10^9
$CuCl_2$	2.8×10^9	3.0×10^9	1.6×10^9	2.1×10^9
TEMPO	1.9×10^9	1.7×10^9	1.3×10^9	1.5×10^9

2 and 3). They all show an intense maximum in the UV region (at 320 nm, with the exception of MSPD, whose peak is centered at 330 nm) and another weaker band in the visible region. The visible absorption appears as a shoulder (430 nm) on the main peak at 320 for PSPD, whereas for the other three molecules, it consists of a resolved band with a well-defined maximum (460, 440, and 460 nm for MSPD, FSPD, and CSPD, respectively). The time evolution of the absorption bands in both UV and visible regions is essentially the same; therefore, only one transient was detected for each PAG, even though a residual absorption was found in the 300−350 range for all four compounds, probably due to photoproduct(s). The kinetic decays of the transients, monitored in the visible region, all follow first-order kinetics, with lifetimes that range from 9.4 μs for CSPD to 18.6 μs for MSPD (Figures 2 and 3, insets). The spectral and kinetic parameters for the transients observed in the laser flash photolysis experiments in N_2-saturated acetonitrile are summarized in Table 1. Although these spectra exhibit many common aspects, they are easily distinguished by the position of the maximum in the visible region. Given that the transient species observed in the photolysis of the four PAGs are not exactly the same, the species cannot be derived from the succinimido radical, formed by the possible homolytic cleavage of N−O bond, which would be the same for all four molecules. Furthermore, if the other species produced in the same process, that is, the arylsulfonate radical, were the species observed in the laser experiments, then this radical should not be affected by oxygen, as is normally observed for oxygen-centered radicals. In contrast with this prediction, our quenching experiments showed that oxygen strongly affects transient lifetimes, with rate constants that vary from 9.8×10^8 M^{-1} s^{-1} (FSPD) to 1.2×10^9 M^{-1} s^{-1} (MSPD and CSPD) (see Table 2).

To characterize the nature of the transients involved in the laser flash photolysis measurements, experiments with various quenchers were performed. The aforementioned rate constants, observed in the experiments with oxygen, suggest that the transient is either a triplet or a radical species. Anthracene (energy of lowest triplet state = 177 kJ mol^{-1})[16] was used to ascertain the possible presence of the PAG triplet state as the species responsible for the transient absorption, but neither an effect on decay lifetime nor a sensitization of the anthracene triplet state was observed for the PAGs; therefore, the transient is not the PAG triplet state. This conclusion is supported by the results obtained in a previous work for another PAG, *N*-oxyphthalimidotrifluoromethylsulfonate (PIT).[10] The triplet−triplet absorption of this molecule is characterized by a narrow band centered at 330 nm. Because the four *N*-oxysuccinimidoarylsulfonate PAGs also contain the same pair of chromophores, that is, phenyl and succinimido rings, but without any conjugation between them, one would expect the triplet state of these PAGs to exhibit the absorption maximum at energy values higher than that observed for PIT.

The presence of a cationic species can also be excluded, on the basis of the initial assumptions and considering the effects of tetrabutylammonium chloride ($Bu_3N^+Cl^-$), an ion-pair reagent with a strong nucleophilic activity because of the Cl^- anions. No effects on transient lifetimes were observed up to a quencher concentration of 3×10^{-3} M.

The effects of hydrogen donors on the transients were also investigated. Benzhydrol (up to a concentration of 2×10^{-3} M), tetrahydrofuran (THF, up to 8 M) and 2-propanol (up to 8 M) were used as potential hydrogen-atom donors, but none of them showed any activity toward the transients for all four *N*-oxysucciminimidoarylsulfonate PAGs. From the concentration used, we can conclude that, if there is any hydrogen-abstraction tendency by the transients, it would be characterized by very low rate constant values ($\leq 10^3$ M^{-1} s^{-1}). These results allow us to rule out the identity of the transients as carbon-centered radicals and succinimido radicals because hydrogen abstraction by these species is well-documented and is expected to occur at faster rates.[17−20]

Another possible reaction pathway is the homolytic cleavage of the O−S bond of the PAGs. This reaction would involve formation of *N*-oxysuccinimido and sulfonyl radicals in the primary step of photoexcitation. The transient absorption spectra cannot be assigned to the first type of radicals because, as we have previously mentioned for the succinimido radicals, they would give exactly the same transient absorption spectra for all PAGs. Additionally, such species are not consistent with our quenching experiments with oxygen. In contrast, sulfonyl radicals could reasonably be responsible for the transient spectra observed in our experiments. The absorption spectra of arylsulfonyl radicals have been characterized in the literature by means of both modulation spectroscopy[21] and conventional flash photolysis[22] and are consistent with the transients obtained here. Some authors[21] observed that para substitution on the phenyl ring does not markedly affect the position of the absorption maximum of the radical because of the light conjugation with the sulfonyl moiety. This is consistent with our observation of only slight differences between the transients of the various PAGs.

We also studied the interaction of the transients observed in the laser experiments with other species such as Cu^{2+} ions ($CuCl_2$) and TEMPO. The rate constants for quenching by $CuCl_2$, toward radical species,[23−25] range from 1.6×10^9 M^{-1} s^{-1} for FSPD to 3.0×10^9 M^{-1} s^{-1} for MSPD, reflecting the oxidizing properties of Cu^{2+} ions.

Quenching by the free radical TEMPO is characterized by rate contants ranging from 1.3×10^9 M^{-1} s^{-1} for FSPD to 1.9×10^9 M^{-1} s^{-1} for PSPD. Although the reactivity of TEMPO toward carbon-centered radicals is well-known,[26,27] its interaction with sulfonyl radicals might seem unusual. However, it is interesting to note that the quenching process by TEMPO radicals leads to a product that is very similar in structure to that of the starting PAG molecules. In addition, the reaction between a stable radical of similar structure (di-*tert*-butyl nitroxide) and a sulfur-centered radical (benzenethiyl radical) has been reported[28] to occur with a rate constant of 1.3×10^9 M^{-1} s^{-1}; therefore the observed behavior is not completely unexpected. The kinetic parameters for quenching by $CuCl_2$ and TEMPO are reported in Table 2, together with the rate constants for quenching by oxygen.

The reaction of sulfonyl radicals with olefins, in particular with vinylic componds, is reported in the literature;[29,30] thus, we decided to try 2,3-dimethyl-1-butene and 3-chloro-2-chloromethyl-1-propene as potential scavengers. No effects were observed up to a concentration of 0.6 M with either olefin; this result indicates that the reactivity of sulfonyl radicals toward vinylic compounds is characterized by rate constants below 10^4 M^{-1} s^{-1}. It should be noted, however, that recent literature reports are mainly concerned with initiation of vinyl polymerization by addition reactions,[30] usually requiring activation of olefins by catalysts; these reactions might therefore occur on a time scale that is too long for the typical time window of laser flash photolysis. Judging from these results, the primary photochemical step for these PAGs is a homolytic

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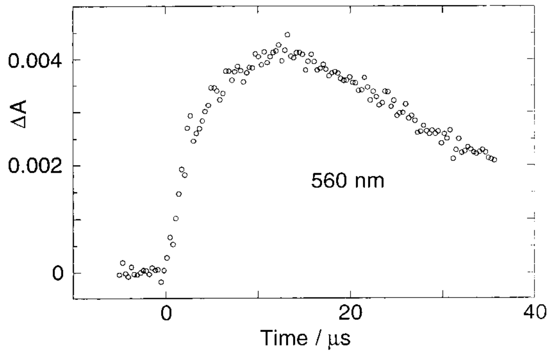
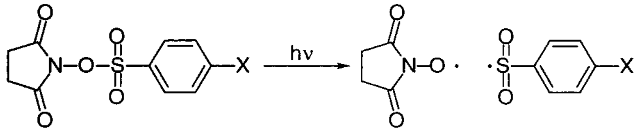


Figure 4. Kinetics of formation and subsequent decay for the transient monitored at 560 nm upon laser flash photolysis of CSPD in O_2-saturated acetonitrile solution.

Scheme 1



cleavage giving rise to *N*-oxysuccinimido radical and an arylsulfonyl radical (see Scheme 1).

In O_2-saturated acetonitrile solution, the arylsulfonyl radicals react with O_2 at slightly below diffusion-controlled rates. In addition to the quenching of these transients by O_2, the formation of another transient species, characterized by different spectral and kinetic behavior, was also observed for all four *N*-oxysuccinimidoarylsulfonate PAGs. The kinetics of formation and subsequent decay for this new species, monitored at 560 nm, is shown in Figure 4 for CSPD. The transient absorption spectra of the four PAGs in O_2-saturated acetonitrile solution (Figures 5 and 6) showed an intense band in the UV region, whose maximum is located below 300 nm, and a second broad band in the visible region, which was centered at 560 nm for MSPD and CSPD and 580 nm for FSPD. This second absorption was difficult to observe for PSPD (Figure 5a), probably because of the lower extinction coefficient of the transient in that spectral range; however, a transient decay with the same characteristics as were found for the other three molecules was observed by averaging a large number of laser shots (Figure 5a, inset). It is important to mention that these transients exhibited a rise time which ranged, for the different PAGs, from 4.8 μs (FSPD) to 9.8 μs (MSPD). Compared to those observed in the N_2-saturated solution experiments, the lifetimes of the transients are now much shorter in O_2-saturated solution, all being around 100 ns. Upon comparison of those lifetimes with the rise times measured for the "new" transients observed in O_2-saturated solution, we notice that they do not match; therefore, we can conclude that the species observed in the N_2-saturated solution experiments, that is, the arylsulfonyl radicals, are not the direct precursors of the new transient detected in the O_2-saturated solutions. Therefore, peroxysulfonyl radicals, which are the presumed products of the reaction between arylsulfonyl radicals and O_2, are not responsible for the new transient. The spectral and kinetic characteristics of the transients observed in O_2-saturated acetonitrile solution are summarized in Table 3.

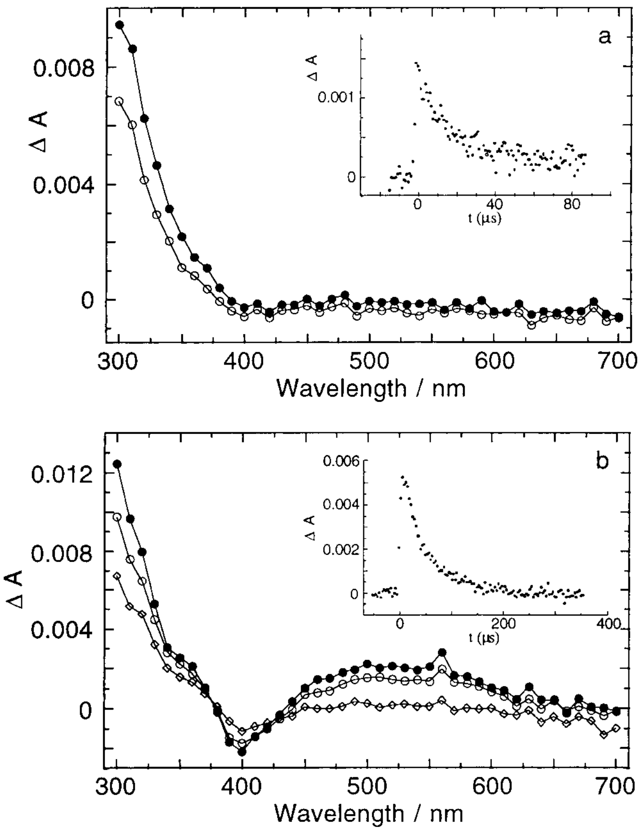


Figure 5. Transient absorption spectra obtained upon nanosecond laser flash photolysis of (a) PSPD and (b) MSPD in O_2-saturated acetonitrile solution. For part a, spectra recorded (●) 9.2 and (○) 65.6 μs after the laser pulse. For part b, spectra recorded (●) 11.2, (○) 33.6, and (◇) 104 μs after the laser pulse. Insets: Decay kinetics monitored at 540 and (b) 560 nm.

We suggest that a consecutive reaction takes place in O_2-saturated solution, through an intermediate species that is transparent in the 300−700-nm range of the laser flash photolysis experiments. In the literature, there are several examples of transient absorption spectra showing the same feature as those found in our experiments that have been assigned to arylperoxy radicals[31−34] formed in air- or O_2-saturated solutions by peroxidation of the corresponding aryl radicals.[30−35] In addition, aryl radicals are known to be transparent in the 300−700-nm spectral range, as they have been reported to have their absorption maxima below 300 nm (260 nm for phenyl radical).[36] Therefore, the transients that we observed in the laser flash photolysis experiments in O_2-saturated solution can be tentatively assigned to the formation of arylperoxy radicals. To confirm these assignments, a series of quenching experiments with *p*-methoxyphenol were carried out with all four PAGs in O_2-saturated solution. *p*-Methoxyphenol[31] and *p*-methoxyphenolate[31] have been reported to act as quenchers of arylperoxy radicals via hydrogen-atom

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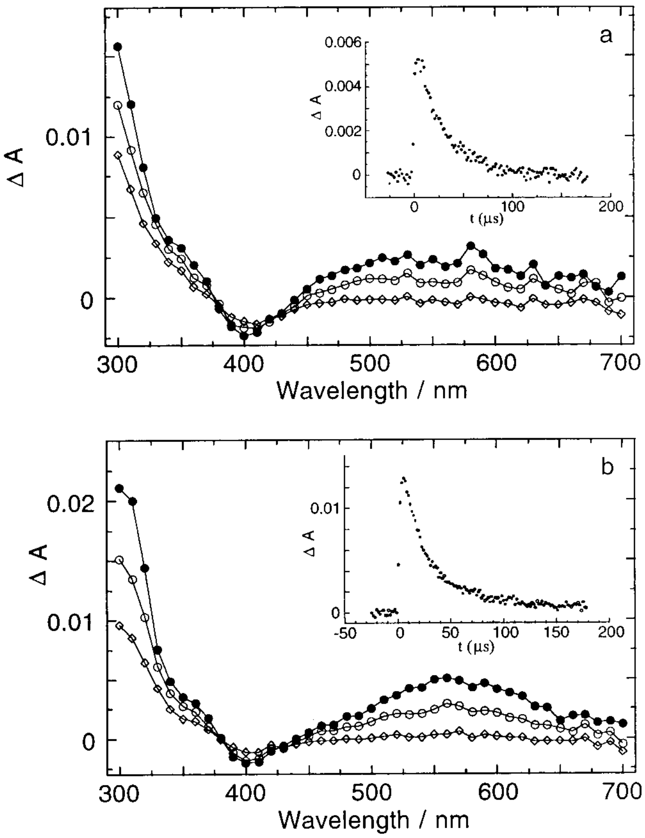

Figure 6. Transient absorption spectra obtained upon nanosecond laser flash photolysis of (a) FSPD and (b) CSPD in O_2-saturated acetonitrile solution. For part a, spectra recorded (●) 9.6, (○) 33.6, and (◇) 94.4 μs after the laser pulse. For part b, spectra recorded (●) 12.8, (○) 43.2, and (◇) 120 μs after the laser pulse. Insets: Decay kinetics monitored at (a) 580 and (b) 560 nm.

Table 3. Spectral and Kinetic Characteristics of the Transients Observed upon Laser Flash Photolysis in O_2-Saturated Acetonitrile Solution (Arylperoxy Radicals and Sulfonyl Radicals)

	arylperoxy			sulfonyl
	λ (nm)	τ (μs)	rise time (μs)	τ (ns)
PSPD	<300	16.1	not measurable	95
MSPD	<300, 560	46.6	9.8	88
FSPD	<300, 580	26.8	4.8	104
CSPD	<300, 560	24.4	5.3	89

donation and electron transfer to the arylperoxy radical, respectively. The rate constants for bimolecular quenching by *p*-methoxyphenol were measured for the four PAGs and found to range from 4.6 × 10^8 M^{-1} s^{-1} for PSPD to 6.9 × 10^8 M^{-1} s^{-1} for CSPD. These values are higher than those normally expected for intermolecular hydrogen-abstraction reactions and higher than that obtained by Alfassi and co-workers,[31] thus suggesting that the mechanism of interaction might involve electron transfer from *p*-methoxyphenol to the arylperoxy radical. The observed formation of the *p*-methoxyphenol radical at 400 nm upon quenching of the arylperoxy radicals occurs via electron transfer followed by proton transfer. To support our suggestion of a possible electron-transfer process being involved in the quenching mechanism by *p*-methoxyphenol, we used triethylamine as a quencher of arylperoxy radicals. Our hypothesis was confirmed by the quenching effect observed, which was characterized by rate constant values with the same order of magnitude as those measured with *p*-methoxyphenol, varying from 4.8 × 10^8 M^{-1} s^{-1} for CSPD to 6.5 × 10^8 M^{-1} s^{-1} for PSPD. The rate constant values for quenching of the arylperoxy radicals are shown in Table 4.

The effects of TEMPO and 2-propanol on the kinetic behavior of these arylperoxy radicals were also studied. The main result observed by using these two quenchers was a drastic reduction of the ΔA of the transients. In contrast, it was impossible to notice any effect on the arylperoxy radicals lifetimes. This effect was not unexpected as a decrease in ΔA indicates an interaction of the quencher with the transient precursor, that is, with the aryl radical. This species is known to be a σ carbon-centered radical,[37–39] and therefore, its lifetime is expected to be reduced by the presence of hydrogen donors, such as 2-propanol (rate constants $k = 1.38 \times 10^6$ and 3×10^7 M^{-1} s^{-1} have been reported, respectively, for the quenching of phenyl radical[40] and 4-hydroxyphenyl radical[41] by 2-propanol) or TEMPO, which is a well-known scavenger of this type of radical.[26,27]

Having established that the transients observed in the laser flash photolysis of the four *N*-oxysuccinimidoarylsulfonate PAGs in O_2-saturated solution can be assigned to the arylperoxy radicals, we must consider how the aryl radicals can be formed from the sulfonyl radicals produced in the primary step of excitation. In the literature, the desulfonylation process has been reported to occur for benzylsulfonyl radicals[42] and α-toluenesulfonyl radicals[43] and in the photodecomposition of arylmethyl sulfones.[44] Additionally, the desulfonylation of an arylsulfonyl radical has been proposed to rationalize some of the products formed in the photolyses of sulfonamide and sulfonate esters,[45] as well as diaryl α-disulfones.[46] Therefore, it is reasonable to conclude that SO_2 loss from the arylsulfonyl radicals is involved in the system currently under consideration.

It is important to note that the values observed for the rise times of the arylperoxy radicals, which range from 4.8 to 9.8 μs (Table 3), are too long to be assigned to the decay of the aryl radicals. In fact, considering the k_q values for the quenching of these species by oxygen measured by Ingold and co-workers[35] in O_2-saturated solution, under our experimental conditions, the aryl radicals should have a lifetime of about 100 ns. Therefore, the rise time values, rather than the reaction of aryl radicals, reflect other distinct processes, that is, the equilibrium between the sulfonyl and the peroxysulfonyl radicals, the fragmentation of the former, and the

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Table 4. Effects of Different Quenchers on Lifetimes of the Transients Observed upon Laser Flash Photolysis in O_2-sSaturated Solution and Assigned to Arylperoxyl Radicals

	k_q (M^{-1} s^{-1})			
	PSPD	MSPD	FSPD	CSPD
p-CH_3O-phenol	4.6×10^8	5.6×10^8	6.7×10^8	6.9×10^8
triethylamine	6.5×10^8	5.4×10^8	5.7×10^8	4.8×10^8
TEMPO	decrease in ΔA	decrease in ΔA	decrease in ΔA	decrease in ΔA
2-propanol	decrease in ΔA	decrease in ΔA	decrease in ΔA	decrease in ΔA

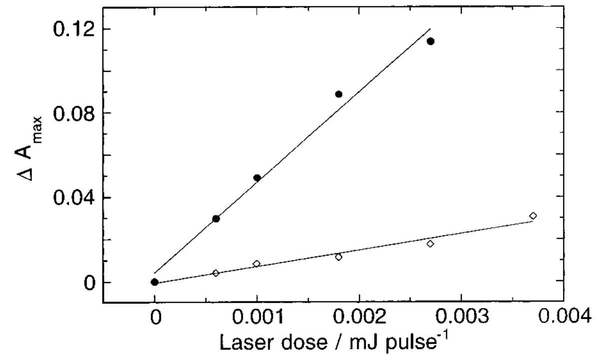
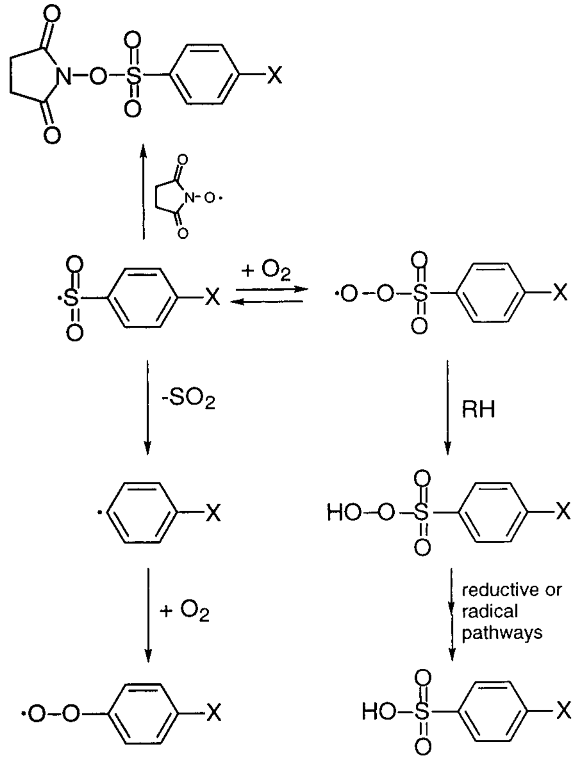


Figure 7. Maximum ΔA values due to Rhodamine B cation, observed at 550 nm, upon laser excitation of (●) MTT and (◊) FSPD in N_2-saturated acetonitrile solution, as a function of laser dose.

Scheme 2



subsequent transformation of the aryl radicals, formed from the sulfonyl radicals by loss of SO_2, into the corresponding arylperoxy radicals (see Scheme 2).[47]

To quantify the photoacid-generating efficiencies of the PAGs, the Φ_{acid} values were measured by means of the nanosecond laser flash photolysis apparatus (see Table 1 and Figure 7). These results are derived from the ability to detect the protonation of an acid sensor, Rb, by an acid sometime after laser excitation of a PAG. This process is not selective and, as such, provides no information concerning the identity of the acid formed. Although acid-generating efficiency is an important parameter for a PAG in terms of usefulness to the microlithographic industry, one must also consider the type of acid being generated. On the basis of the results presented to this point, one is tempted to suggest that the acid formed by these PAGs is sulfurous acid, formed by the reaction of SO_2 with water.

Table 5. Quantum Yield Data for MSPD under Steady-State Conditions

purging gas	Φ_{acid}	Φ_{PTSOH}	Φ_{decomp}
N_2	0.15	0.20	0.18
O_2	0.38	0.32	0.32

To further investigate the nature of the acid formed, product studies were performed after the steady-state photolysis of MSPD. Analysis of the product mixtures formed in solutions purged with N_2 and O_2 by LC/MS reveals the main products to be *N*-hydroxysuccinimide and *p*-toluenesulfonic acid (PTSOH), as determined from the *m/z* values and characteristic fragmentation patterns, respectively. In the presence of O_2, PTSOH is presumably formed by the reaction of the peroxy radical derived from the quenching of the arylsulfonyl radical by O_2 with a hydrogen donor. The peroxyacid thus formed can undergo facile thermal homolytic O−O cleavage to yield an oxygen-centered radical that reacts with a hydrogen donor to yield PTSOH (see Scheme 2) or to be reduced to the acid during handling. In the solutions purged with N_2, there might be traces of residual O_2 present that make this pathway viable. Alternatively, the disproportionation of arylsulfonyl radicals has been suggested as a route to sulfonic acid formation.[45] It should also be noted that sulfonic acids have been identified as products in the absence of O_2 in other photoreactions in which arylsulfonyl radicals have been implicated.[46]

The Φ_{acid}, Φ_{PTSOH}, and Φ_{decomp} values were determined under conditions of steady-state irradiation in solutions purged with N_2 and O_2 and appear in Table 5. In both cases, Φ_{acid} is essentially the same as Φ_{PTSOH}, indicating that PTSOH is the only acid formed in significant yield. The fact that the Φ_{decomp} values are also very similar to the Φ_{PTSOH} values indicates that, for every PAG molecule destroyed by photolysis, a PTSOH molecule is formed. This can be the case only if the desulfonylation reaction, observed in LFP, is either a very minor process or reversible.

Given the importance of O_2 in the reaction path, it is not surprising that the quantum yields are larger in solutions purged with O_2 than in those purged with N_2. In solutions purged with N_2, the Φ_{decomp} values are also

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[47] Subsequent experiments in our lab on diaryl α−disulphones, which yield arylsulfonyl radicals upon irradiation (see ref 22 and references therein) confirm that the behavior observed in the LFP of *N*-oxysuccinimidoarylsulfonate PAGs is due to the formation of arylsulfonyl radicals in the primary photochemical step.

very similar to the Φ_{PTSOH} values, yet both are lower than the corresponding values in O_2-purged solutions. This indicates the presence of a pathway that competes with trapping of the arylsulfonyl radical by O_2 but does not result in a decomposed PAG molecule. We suggest that this pathway is the recombination of the arylsulfonyl radical and the *N*-oxysuccinimide radical to regenerate starting material. This process is expected to be more prevalent in the O_2-depleted environment of a solution purged with N_2 than in a solution purged with O_2 and, therefore, accounts for the observed reduction in acid production. The complete mechanism of reaction of the arylsulfonyl radicals can therefore be summarized as shown in Scheme 2.

The reaction of the *N*-oxysuccinimido radical with the arylsulfonyl radical also needs to be invoked to explain the result that the Φ_{acid} values are higher in steady-state experiments than in experiments that employ laser excitation. The greater photon fluence present in a laser experiment as compared to a lamp results in a corresponding increase in the concentration of reaction intermediates formed in the light path. A higher concentration of the radicals produced in the reactions currently under consideration would certainly enhance a radical−radical combination pathway, thereby reducing the yield of acid produced via a competing pathway. Similar effects resulting from an enhancement of radical−radical combination pathways under laser irradiation are well-established. Although this phenomenon can result in the formation of different products under laser and lamp irradiation, there is no need to consider the possibility of different acids being formed under differing irradiation conditions in the reactions of the PAGs currently under consideration. The competition between the desulfonylation reaction of arylsulfonyl radicals, which can conceivably yield sulfurous acid, and reaction with O_2, which is the first step in the generation of a sulfonic acid, should be unperturbed by the differing concentrations of radical species that result from different light sources.

Conclusion

Irradiation of *N*-oxysuccinimidoarylsulfonate PAGs leads to homolytic cleavage of the S−O bond of these molecules and subsequent production of arylsulfonyl radicals. Laser flash photolysis indicates that these species can undergo desulfonylation, thereby generating SO_2 and aryl radicals, which, in O_2-saturated solution, are converted into arylperoxy radicals. Steady-state irradiations indicate that the acids generated by these PAGs are sulfonic acids that are formed via a reaction pathway that begins with the reaction of arylsulfonyl radicals with O_2. If other acids are formed, such as sulfurous acid, their yields have to be sufficiently small that, within experimental error, they do not interfere with the mass balance.

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