Model Studies on the Photochemistry of Phenolic Sulfonate Photoacid Generators

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Received January 27, 1998

The mechanism of photodissociation and acid generation for three phenolic sulfonate esters, ranging from alkyl, to benzylic, to aromatic, was investigated by laser flash photolysis and product studies. All the sulfonate esters studied showed the presence of phenoxy and other complex radicals in the transient spectra. The formation of these complex transients indicates that the radical pair formed upon excitation of the sulfonate can escape the solvent cage, and undergo further chemical transformations. It was observed that all of the sulfonate esters investigated resulted in the formation of acidic species. Photoproduction studies indicate that phenyl methanesulfonate and phenyl toluene-p-sulfonate undergo a photo-Fries type rearrangement and also produce a large excess of phenol with the corresponding sulfonic acid. Upon excitation, phenyl toluene-o-sulfonate undergoes near quantitative SO2 extrusion, with the formation of no Fries rearrangement photoproducts; instead it was observed that the benzylic radicals, generated by SO2 loss, undergo a “pseudo” Fries rearrangement to form the ortho and para phenylmethane isomers. Further, the SO2 photogenerated undergoes oxidative and hydrolytic processes to form sulfuric and sulfurous acids.

Introduction

Molecules which generate acid upon exposure to radiation have been extensively investigated in microlithography.1,2 The photodissociation of sulfonate esters has been widely used to generate acid. Several classes of sulfonate esters have been utilized as photoacid generators (PAGs) in chemically amplified photoresists.3 These include the o-nitrobenzyl4 and p-nitrobenzyl5 sulfonate esters which, via different photochemical mechanisms, undergo C-O bond cleavage to generate sulfonic acid. Another interesting class of PAGs is the multifunctional phenolic sulfonates.6 It was reported that as the number of sulfonate esters bonded to the aromatic ring is increased there is a concomitant increase in the efficiency of acid generation (the molar ratio of sulfonate esters groups being normalized to 1).7 For example, the sulfonate esters of 1,2,3-trihydroxybenzene are more efficient at generating acid than the corresponding esters of 1,2-dihydroxybenzene, which in turn is more efficient than the sulfonate ester of phenol. However, no satisfactory photochemical mechanism has been described to account for acid generation from this type of molecule.

It has been previously reported that phenolic sulfonate esters undergo the photo-Fries rearrangement, in which the sulfonyl moiety migrates to the ortho and para positions of the phenolic ring.8 In addition to this intramolecular rearrangement, side reactions occur resulting in the formation of phenol and unidentified byproducts. It is believed that the mechanism of the photo-Fries rearrangement of sulfonate esters is analogous to that of carboxylic acids,9 that is, the homolytic cleavage of the S-O bond to form a radical pair [ArO + SO2R], in the solvent cage, which then undergoes intramolecular coupling or cage escape. For acid or phenol to be formed, these radicals must escape from the solvent cage and undergo side reactions, such as hydrogen abstraction. For example, it has been reported that the photolysis of phenyl benzenesulfonate in acetonitrile at 67% conversion results in the formation of ~24% of the photo-Fries ortho and para products, ~11% of phenol, and ~65% of unknown products.9 That is, the major outcome of the photolysis of phenyl benzenesulfonate are non-Fries rearrangement products. Thus, escape from the solvent cage and the
resultant side reactions of these radicals play a major role in determining the final product distribution. However, to the best of our knowledge, no detailed study of these side reactions and their involvement in acid formation has been reported.

This paper reports an investigation of the solution photolysis of three model compounds ranging from alkyl to benzylic to aromatic sulfonates: phenyl methanesulfonate (1), phenyl toluene-α-sulfonate (2), and phenyl toluene-p-sulfonate (3). Scheme 1. The objective of this study was to model the photodecomposition of this type of sulfonate ester in solution. However, it is noted that the mechanism of photolysis of these sulfonates in a polymer matrix, such as a photoresist, maybe quite different. Detailed photoproduct studies on irradiated acetonitrile solutions of these compounds were undertaken using gas chromatography-mass spectrometry. Ion chromatography and potentiometric titrations were used to quantify and identify the acid formed from these sulfonate esters. Further, the transient species formed during the photolysis of these sulfonate esters were studied by nanosecond time-resolved laser flash photolysis.

**Experimental Section**

**Synthetic Procedures.** Phenyl Methanesulfonate (1). To a solution of phenol (25.0 g, 0.266 mol) and triethylamine (40.3 g, 0.398 mol) in dry acetonitrile (250 mL) was added methanesulfonyl chloride (33.5 g, 0.292 mol) dropwise at 0–8 °C under nitrogen. After addition of methanesulfonyl chloride, the reaction mixture was stirred at <5 °C for 2 h under nitrogen. The reaction was then filtered and the filtrate precipitated into 500 mL of a 5% hydrochloric acid solution with vigorous stirring. The resulting white solid was filtered and washed well with deionized water. The white solid was then slurried twice in 250 mL of deionized water and then dried in a vacuum oven overnight. Yield 39.47 g (86% of theory) of the title compound having a melting point of 65 °C (peak temp, DSC/20 °C min) (lit. mp 65 °C).10 1H NMR of (1) (CDCl3): δ 3.07 (3H, s, CH3), 7.19–7.51 (5H, m, aromatic). 1R of (1) (KBr disk, cm−1): 1350 and 1181 (SO2). MS of (1): m/e 172 (M+).

Phenyl Toluene-α-sulfonate (2). Yield 92.5% of theory of the title compound having a melting point of 92 °C (peak temp, DSC/20 °C min) (lit. mp = 87 °C).11 1H NMR of (2) (CDCl3): δ 4.50 (2H, s, CH2), 7.05–7.57 (10H, m, aromatic). 1R of (2) (KBr disk, cm−1): 1350 and 1181 (SO2). MS of (2): m/e 248 (M+).

Phenyl Toluene-p-sulfonate (3). Yield 91.8% of theory of the title compound having a melting point of 99 °C (peak temp, DSC/20 °C min) (lit. mp = 92–95 °C).12 1H NMR of (3) (CDCl3): δ 2.42 (3H, s, CH3), 6.96 (2H, d, aromatic), 7.26 (5H, m, aromatic), 7.67 (2H, d, aromatic). 1R of (3) (KBr disk, cm−1): 1354 and 1183 (SO2). MS of (3): m/e 248 (M+).

**Laser Flash Photolysis.** The experimental setup used for the laser flash photolysis studies is very similar to that described in detail previously.13 Sulfonate ester concentrations in acetonitrile ranged from 1.5 × 10−3 to 5 × 10−5 M. Photolysis was carried out in a continuous flow quartz cell connected to a solution reservoir where the solution was saturated by a slow stream of nitrogen or oxygen. Transient absorption spectra were recorded from 280 to 700 nm, typically in the microsecond time scale, and sample decay traces were recorded at the appropriate transient absorption bands. Further details can be found elsewhere.13

**Product Studies.** Photolysis of the sulfonates 1, 2, and 3 were performed in acetonitrile in the 0.005–0.006 M concentration range using 20 mL quartz test tubes. These solutions were purged with either nitrogen or oxygen for 10 min prior to irradiation. Irradiations were carried out in a Rayonet photoreactor using 8 RPR-254 lamps emitting predominantly at 254 nm. Exposure times of 15 and 60 min were used, yielding typical conversions greater than 30% and 50%, respectively. Photolysis products were analyzed by gas chromatography (GC) using a DB-5 column, 30 m × 0.32 mm (J&W Scientific). GC conditions: injection volume 1 μL; initial temperature 70 °C, 2 min; ramp rate 70–280 °C, 20 min; final temperature 280 °C, 5 min. The identity of the photoproducts was determined by GC/MS analysis and in most cases verified by injection of the authentic material. GC for each solution was run in triplicate, and average areas were calculated for each peak and compared with those for an internal standard (dodecane). Using these data the average percent conversion of starting material to photoproducts was obtained and the relative product ratios were determined, Table 1.

A similar irradiation procedure was used to investigate photolysis formation from these sulfonates in acetonitrile. For each sulfonate (1, 2, and 3), the solutions (0.005 M, 20 mL) were irradiated for 5, 10, 20, 30, and 40 min, under nitrogen. Known volumes of these irradiated solutions were diluted to 110 mL with deionized water. The extent of photolysis generation was determined by titration with 0.0201 M sodium hydroxide. Potentiometric titrations were performed using a Metrohm combination glass pH electrode in conjunction with a Brinkmann 665 Dosimat and a Brinkmann 682 Titro

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**Table 1. Photolysis of Phenyl Methanesulfonate (1)**

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*a Fifteen minutes photolysis. *b Sixty minute photolysis.
processor. Ion chromatography was performed using a AS 10 Dionex column with 10% acetonitrile in 0.1 N sodium hydroxide solution as eluent. Anion group tests were carried out to determine sulfate and sulfite anions using barium nitrate, according to the literature procedure.14

Results and Discussion

Laser Flash Photolysis. Laser flash photolysis (LFP) (266 nm) of 1 in nitrogen-saturated acetonitrile solutions leads to the unequivocal detection of phenoxyl radical. The transient spectra of 1 exhibits a strong absorption with a $\lambda_{\text{max}}$ at ca. 400 nm indicative of the phenoxyl radical (Figure 1).15 The behavior of the phenoxyl radicals was monitored at 400 nm and shows a complex decay, with a half-life of ca. 1 $\mu$s (Figure 1, inset). The half-life of this transient is too short for a phenoxyl radical, therefore suggesting that its decay involves reactions with other radicals generated in the system.

Excitation of 2 at 266 nm leads to the detection of not only phenoxyl radicals (ca. 400 nm) but also benzyl radicals, which are well-known to have a $\lambda_{\text{max}}$ ca. 316 nm (Figure 2).16 Interestingly the benzyl radicals are rather short-lived, suggesting that their decay is dominated by reactions with other, probably more persistent,17 species (Figure 2, inset). Further, when acetonitrile solutions of 2 are saturated with oxygen, the effect on the phenoxyl radicals is minimal, but the characteristic peak due to the benzyl radicals is no longer detectable (Figure 3). The failure to detect benzyl radicals from 2 in the presence of $O_2$ is expected, given their high reactivity toward oxygen,18 and is consistent with the formation of oxidation products, vide infra.

Laser excitation (266 nm) of 3 leads to readily detectable signals from phenoxyl radicals centered around 400 nm, along with signals from a shorter lived radical that we tentatively assign to $p$-CH$_3$C$_6$H$_4$SO$_2$·; additional signals in the 320–340 nm region probably incorporate contributions from this radical (Figure 4). The detection of phenoxyl and other complex radicals in the transient spectra of all three of these sulfonates, 1, 2, and 3, indicates that the radical pair formed upon excitation escapes the solvent cage, and can therefore undergo further transformations leading to the generation of acid, Scheme 2.
**Photoacid Generation.** The photoliberation of acid via the formation of non-Fries rearrangement products and subsequent side reactions was investigated for the three sulfonate ester model compounds, 1, 2, and 3. Photolysis experiments were performed in nitrogen saturated acetonitrile, using a Rayonet photoreactor (8 lamps with λexc 254 nm). The photoliberation of acid was determined by potentiometric titration using 0.0201 N NaOH. It was observed that the photolysis of all of the model sulfonate esters, 1–3, resulted in the formation of acidic species. The relative efficiency of photoacid generation from 1, 2, and 3 was quantified as a function of exposure dose. As can be seen from Figure 5, increasing photolysis time causes a concomitant increase in the concentration of acid generated for all these sulfonates. Of the three compounds studied, the benzyl sulfonate (2) was by far the most efficient at generating acid. Sulfonate 2 generated approximately twice the concentration of acid relative to phenyl methanesulfonate (1) and phenyl toluene-p-sulfonate (3), at all exposure doses. Of sulfonates 1 and 3, the methanesulfonate (1) was slightly more efficient at generating acid than the toluene-p-sulfonate (3). In contrast to the acid–base titration behavior of 1 and 3, which liberate acids of similar pKₐ values, the titration curves obtained from the photolysis of 2 exhibit two distinct end points. Parts a and b of Figure 6, illustrate the titration curves for 2 and 3, respectively, with increasing photolysis time. The existence of two distinctive pKₐ values for 2 can be attributed to either the presence of a diprotic acid or the generation of a strong and weak acid. In an effort to understand the differences in acid-generating behavior between these three sulfonates, photoproduct studies were undertaken to identify and quantify the photoproducts generated from these compounds. GC–mass spectroscopy was used to identify the neutral photoproducts resulting from the photolysis of sulfonates 1, 2, and 3. Ion chromatography (IC) and anion group tests for sulfate and sulfite were performed to analyze the acidic species photogenerated.

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**Scheme 2. Proposed Mechanism of Photoacid Generation**

![Diagram of proposed mechanism](image)

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**Figure 5.** Relative photoacid generation efficiency for sulfonate esters 1–3.

**Figure 6.** Potentiometric titration curves for (a) 2 and (b) 3 with increasing exposure dose.

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Fries product was observed, while at higher conversions both the ortho and para Fries products were detected. An oxygen atmosphere had no effect on the type of photoproducts formed but did affect the product ratio at higher conversions compared to photolysis in a nitrogen environment. In the presence of oxygen the quantity of phenol was reduced relative to the photo-Fries rearrangement products. The photoproduct distribution ratio shows that excess phenol was present, indicating that the phenoxyl radical formed upon photolysis of 1 can escape the solvent cage and eventually lead to phenol. The detection of phenol is in agreement with the phenoxyl transient observed by laser flash photolysis, vide supra. Further, an excess of phenol implies that an equivalent quantity of the methane-
sulfonyl radical escapes from the solvent cage. Photoliberation of acid from 1 also indicates that the sulfonyl radical undergoes side reactions, such as proton abstraction, to form acidic species. Using ion chromatography, methanesulfonic acid was detected in the photolyzed solution of 1.

Phenyl Toluene-α-sulfonate (2). The photoproduct distribution observed for the benzylsulfonate ester (2) was complex compared to that of the methanesulfonate ester (1), due to SO2 extrusion (Table 2). The formation of benzyl radicals from 2 is evident from the LFP transient spectra, which contain a characteristic absorption at ~316 nm. Further, GC/MS showed no evidence for the formation of any “classical” Fries rearrangement products from 2. The major products observed, 1-hydroxyphenyl-2-phenylmethane and 1-hydroxyphenyl-4-phenylmethane, are the result of SO2 loss, either directly during photolysis of 2 or from the benzylsulfonyl radical formed during photolysis. In a fashion similar to the desulfonylation of the benzylsulfonyl radical shown above, it has been reported that the analogous phenylacetyl radical will undergo photo-decarbonylation to generated benzyl radical. The benzyl radical formed by SO2 loss undergoes a “pseudo” Fries rearrangement to form the ortho and para phenylmethylene isomers observed. A number of other products are formed via the reaction of this benzyl radical. Small quantities of diphenylethane are formed by the recombination of two benzyl radicals. Also the benzyl radical reacts directly with the phenoxyl radical to form 1-phenoxy-1-phenylmethane. In an oxygen environment, two further oxidation products of the benzyl radical are observed, benzoaldehyde and benzyl alcohol. The formation of these by-products illustrates the reactive nature of this radical and may account for the short half-life of the benzyl transient. Further, the disappearance of the signal for the benzyl transient in the presence of oxygen may be due to the formation of these oxidation products, vide supra. A mass balance of the photoproducts from the photolysis of 2 indicates that the vast majority of the benzyl moiety is accounted for, and therefore little or no benzensulfonic acid can be present. This was confirmed by IC which detected no benzyl-

**Table 2. Photolysis of Phenyl Toluene-α-sulfonate (2)**

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| 12 (N2)¹ | 7 | -- | -- | 42 | 25 | 6 | 20 |
| 46 (N2)² | 14 | -- | -- | 42 | 29 | 5 | 10 |
| 24 (O2)¹ | 14 | 13 | trace | 35 | 20 | trace | 18 |
| 44 (O2)² | 13 | 13 | 5 | 28 | 25 | trace | 16 |

¹ Fifteen minutes photolysis. ² Sixty minute photolysis.

sulfonylic acid in photolyzed solutions of 2. However, as shown previously, 2 was by far the most efficient photoacid generator of the three sulfonate esters investigated. This may be accounted for by the fact that upon photolysis all the SO2 is extruded and subsequently undergoes reactions to form acid, as either H2SO3 or H2S2O4. This is supported by the observation that the photolyzed solutions of 2 had a strong odor, indicative of sulfur dioxide. Qualitative tests for SO2 using acidic aqueous KMnO4 stained paper strips, gave a positive test, confirming the presence of SO2. The photogenerated SO2 in the presence of water can form sulfurous and sulfuric acid. The presence of sulfate and/or sulfite oxidation products was confirmed by anion group tests using barium nitrate. Further, the two distinct end points observed in the titration curves of 2 may be accounted for by the presence of these strong and weak acids, sulfuric acid (pKₐ = −3.0) and sulfuric acid (pKₐ = 1.89).²⁰

Phenyl Toluene-p-sulfonate (3). As was observed for 1 and 2, LFP indicates the presence of phenoxyl radicals in the transient spectra for 3. The photoproduct distribution ratio obtained for 3 also indicates that free phenol is present, Table 3. The transient spectra for 3 contained a short-lived radical, which we tentatively assigned to p-CH3C6H4SO2H. p-Toluene sulfonic acid was observed by ion chromatography in photolyzed solutions of 3, indicating that the p-toluene sulfonyl radical upon escape from the solvent cage undergoes reaction with water.

As was found to be the case for phenyl methane-sulfonate (1), at low conversion only the ortho Fries product was detected in the photolyzed solutions of 3, in both O2 and N2 environments. At higher conversion, in N2, only a trace of the para isomer was observed for 3. However, at this higher conversion, two unexpected photoproducts were found for 3 by GC/MS, which we preliminarily assign as diphenyl sulfide and phenyl toluene-p-sulfide. In an O2 environment these two reduction products were not present, and in contrast to a N2 atmosphere, the para Fries product was observed in substantial quantities. Further, in an O2 atmosphere, the quantity of Fries rearrangement products


was greatly increased relative to free phenol, compared to a N₂ environment.

Interestingly, a further non-Fries rearrangement photoproduct was observed in the photolyzed solutions of 3, in both N₂ and O₂ atmospheres, 1-methyl-4,4'-diphenyl (4). The most likely mechanism for the formation of 4 is SO₃ extrusion from 3, Scheme 3. Direct SO₃ loss from sulfonate esters, and the subsequent recombination of the resultant radicals, has been previously reported for p-nitrobenzyl-9,10-dimethoxyanthracene-2-sulfonate. It was observed that this sulfonate photochemically dissociates via an intramolecular electron-transfer process, which leads to heterolytic C-O bond cleavage. This is in contrast to homolytic S-O bond cleavage in the case of a photo-Fries type dissociation. The resultant sulfonate anion then undergoes SO₃⁻ loss, forming the phenyl radical which can recombine with other radicals or react with the solvent in the photolyzed solution. A similar heterolytic C-O bond cleavage may account for the formation of 4 from phenyl toluene-p-sulfonate (3).

It should be noted that the SO₃ extruded from 3 will react to form sulfuric acid in the presence of water.

Further, two end points were not observed in the titration curves for 3 (Figure 6b), indicating the presence of sulfuric acid and p-toluenesulfonic acid, due to the similar dissociation constants for these two acids under the experimental conditions used.

**Conclusions**

This investigation into the photochemistry of phenolic sulfonates indicates that very simple sulfonate esters, such as 1, 2, and 3, can act as efficient photoacid generators. The photoliberation of acid from these esters can be accounted for by escape of the transient species from the solvent cage and their subsequent reaction. This mechanism is supported by the detection of phenoxy and benzyl radicals in the transient spectra of 1, 2, and 3. Further, product studies indicate that in all three cases a large excess of non-Fries rearrangement products are formed, which also supports the formation of acidic species.

**Acknowledgment.** Financial support by the Natural Sciences and Engineering Council of Canada through an operating Grant (J.C.S.) is gratefully acknowledged. We also acknowledge Mike O’Leary and Cathie Swible-Keane for help with potentiometric titrations and ion chromatography.