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Efficient Photoacids Based upon Triarylamine Dialkylsulfonium Salts

Wenhui Zhou, Stephen M. Kuebler, Dave Carrig, Joseph W. Perry,* and Seth R. Marder*

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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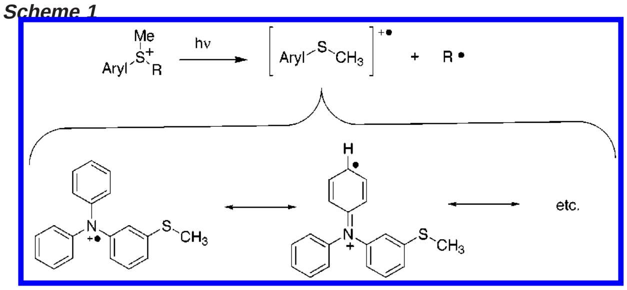
Abstract: New triarylamine dialkylsulfonium salts that are photosensitive in the near-ultraviolet have been prepared. The quantum yields of photoacid generation were found to be ~0.5 and are independent of the counterion. On the other hand, the efficiencies of the sulfonium salts toward the photopolymerization of cyclohexene oxide depend on the counterion and the sulfonium substituents. Photopolymerization kinetic studies demonstrate that these triphenylamine sulfonium salts are highly efficient cationic photoinitiators.

Introduction

Photoacids are used extensively in both positive- and negative-tone photoresist formulations in the microelectronics industry.[1] In particular, iodonium and sulfonium salts have found widespread use as initiators for cationic photopolymerization of epoxides and vinyl ethers,[2] and for the cleavage of *tert*-butoxycarbonyl, *t*-BOC, esters in chemically amplified resists.[3] Saeva[4] has shown that for arylsulfonium salts, the photofragmentation can be initiated either by direct excitation of a $\pi-\sigma^*$ (sulfur−carbon bond) transition or by excitation of a $\pi-\pi^*$ transition followed by intramolecular electron transfer to the σ^* orbital of the sulfur−carbon bond. In both cases, subsequent homolytic cleavage of the sulfur−carbon bond leads to formation of a cation-radical on the sulfur-containing fragment, and a neutral radical (Scheme 1, top). These species undergo secondary reactions, such as radical coupling or H-transfer, to produce Brønsted acid, which are important in the decomposition of some sulfonium salts. In the past, this reaction has been facilitated by stabilizing the radical fragment.[4−7] In contrast, phenyldimethyl sulfonium salts having a σ^* LUMO are not photoactive toward acid generation. This has been attributed to the strength of the $S-CH_3$ bond (or, in other words, the instability of a methyl radical), which allows radiative and nonradiative decay pathways to compete effectively with C−S bond cleavage.[6] Provided that the energy of the excited state is sufficient enough to populate σ^*, it then follows from the Hammond postulate that both the driving force and rate for bond homolysis should be strongly affected by the stability of *both* the radical cation and the neutral radical. Herein, we explore the hypothesis that the quantum efficiency of photoacid generation can also be enhanced by incorporating triarylamine functionalities that stabilize the radical cation intermediate formed upon homolysis of the carbon−sulfur bond of aryl dialkyl sulfonium salts (Scheme 1, middle and bottom). Triarylamine sulfonium salts were selected as the initial targets to test our hypothesis because (i) triarylamine radical cations are known to be very stable; (ii) protonated triarylamino groups are extremely strong acids (Ph_3N^+H, $pK_a = -5$),[8] thus the presence of this amine functionality should not inhibit reactions such as the ring-opening polymerization of epoxides; and (iii) the conditions used in the preparation of aryl dialkyl sulfonium salts[9] are compatible with those of the triarylamine functional group.

Scheme 1



Experimental Section

Absorption spectra were recorded on a Hewlett-Packard model 8453 spectrophotometer. Fluorescence spectra were collected on a Jobin Yvon Spex Fluorolog-III fluorimeter. Gas chromatography−mass spectrometry spectra were obtained on a Hewlett-Packard model 6890

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GC system with a model 5973 mass selective detector. NMR spectra were recorded on a Varian Unity Plus-500 (500 MHz) spectrometer. Combustion elemental analyses were performed by Desert Analytics. Standard reduction potentials were measured on a BAS Model 100B/W cyclic voltammetry unit. A glassy-carbon electrode was used as the working electrode along with a platinum auxiliary electrode and a standard Ag/AgCl reference electrode. Spectrophotometric grade acetonitrile (Aldrich) was used as received in the measurement of absorption and fluorescence spectra. Triphenylsulfonium hexafluoroantimonate (**10**) was synthesized following a literature procedure[10] and recrystallized from 2-propanol. Phenyl dimethylsulfonium triflate was synthesized following a literature procedure.[9] All other commercially available reagent grade chemicals were obtained from Aldrich and used without further purification.

Preparation of 3-Bromothioanisole (1). 3-Bromobenzenethiol (5.0 g, 26.44 mmol) was added to a solution of sodium methoxide (1.43 g, 26.48 mmol) in 20 mL of anhydrous methanol. The mixture was stirred for 30 min under nitrogen at room temperature and then a solution of methyl iodide (4.51 g, 31.77 mmol) in 20 mL of anhydrous methanol was added dropwise. The reaction mixture was stirred overnight under nitrogen at room temperature, poured into 2 M aqueous sodium hydroxide, and extracted with ether (3 × 50 mL). The combined organic layer was washed with saturated brine and dried over anhydrous magnesium sulfate. After removal of solvent, the product was purified by distillation at 80 °C (0.3 mmHg) to give 4.2 g of a colorless oil (86.1%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (s, br, 1H), 7.26 (d, br, 1H), 7.12−7.20 (m, 2H), 2.50 ppm (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.9, 130.0, 128.6, 127.9, 124.9, 122.9, 15.6 ppm. Electron ionization mass spectrometry (EIMS, rel intensity %) 202, 204 (1:1, 100, M^+).

Preparation of 3-Bromophenyl Benzyl Sulfide (2). 3-Bromobenzenethiol (5.0 g, 26.44 mmol) was added to a solution of sodium methoxide (1.43 g, 26.48 mmol) in 20 mL of anhydrous methanol. The mixture was stirred for 30 min at room temperature under nitrogen and then a solution of benzyl bromide (4.53 g, 26.48 mmol) in 20 mL of anhydrous methanol was added dropwise. The reaction mixture was stirred overnight under nitrogen at room temperature, poured into a 2 M aqueous solution of sodium hydroxide, and extracted with ether (3 × 60 mL). The combined organic layer was washed with saturated brine and dried over anhydrous magnesium sulfate. After removal of solvent, the product was purified by distillation at 161 °C (0.3 mmHg) to give 6.31 g of colorless oil (85.5%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (t, J = 1.7 Hz, 1H), 7.27−7.35 (m, 5H), 7.26 (m, 1H), 7.02 (dt, J = 8.0, 1.5 Hz, 1H), 7.11 (t, J = 8.0 Hz, 1H), 4.17 ppm (s, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 136.7, 131.7, 130.1, 129.2, 128.8, 128.6, 127.8, 127.4, 122.6, 38.7 ppm. EIMS (rel intensity %) 278, 280 (1:1, 30.8, M^+).

Preparation of 3-Methylthiotriphenylamine (3). 3-Bromothioanisole **(1)** (2.0 g, 9.85 mmol) was added to a solution of tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) (0.28 g, 0.306 mmol) and bis(diphenylphosphino)ferrocene (DPPF) (0.245 g, 0.442 mmol) in dry toluene (20 mL) under nitrogen atmosphere at room temperature. The resultant mixture was stirred for 10 min. Sodium *tert*-butoxide (2.17 g) and diphenylamine (1.67 g, 9.85 mmol) were then added and stirred at 90 °C for 24 h. The reaction mixture was poured into 20 mL of water, extracted three times with ether (3 × 60 mL), and dried over anhydrous magnesium sulfate. The product was purified by flash column chromatography with use of 2% ethyl acetate in hexanes as eluent to give 1.87 g of a pale yellow oil (65.2%). The purity of the product was estimated greater than 95% by ^{1}H NMR and was used in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, br, J = 7.5 Hz, 4H), 7.14 (t, J = 8.2 Hz, 1H), 7.08 (d, br, J = 8.2 Hz, 4H), 7.02 (t, br, J = 7.5 Hz, 2H), 6.97 (t, J = 2.0 Hz, 1H), 6.87 (d, br, J = 8.0, 1H), 6.82 (d, br, J = 8.0, 1H), 2.20 ppm (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 147.5, 139.3, 129.4. 129.2, 124.3, 122.9, 121.5, 120.5, 120.2, 15.6 ppm. EIMS (rel intensity %) 291 (100, M^+).

Preparation of 3-Benzylthiotriphenylamine (4). 3-Bromophenyl benzyl sulfide **(2)** (1.86 g, 6.67 mmol) was added to a solution of tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) (0.15 g, 0.16 mmol) and bis(diphenylphosphino)ferrocene (DPPF) (0.11 g, 0.20 mmol) in dry toluene (20 mL) under nitrogen atmosphere at room temperature. The resultant mixture was stirred for 10 min. Sodium *tert*-butoxide (1.42 g) and diphenylamine (1.13 g, 6.69 mmol) were then added to this solution which was stirred at 90 °C for 24 h. The reaction mixture was poured into 20 mL of water, extracted three times with ether (3 × 60 mL), and dried over anhydrous magnesium sulfate. The product was purified by flash column chromatography with use of 2% ethyl acetate in hexanes as eluent to give 1.53 g of a pale yellow oil (62.5%). The purity of the product was estimated greater than 95% by ^{1}H NMR and was used in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.2−7.3 (m, overlap, 9H), 7.10 (t, J = 8.0 Hz, 1H), 7.0−7.06 (m, overlap, 7H), 6.93 (d, br, J = 8.0 Hz, 1H), 6.86 (d, br, J = 8.0 Hz, 1H), 4.04 ppm (s, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 147.4, 137.4, 137.2, 129.4, 129.2, 128.7, 128.4, 127.1, 124.4, 123.4, 123.0, 121.6. 38.7 ppm (one carbon was not observed). EIMS (rel intensity %) 367 (100, M^+).

Preparation of [3-(*N,N*-Diphenyl)amino]phenyl Dimethyl Sulfonium Trifluoromethanesulfonate (5). 3-Methylthiotriphenylamine **(3)** (1.77 g, 6.08 mmol) was dissolved in 30 mL of dry methylene chloride and cooled to −78 °C in the dark. To this solution was added via syringe 0.76 mL (1.10 g, 6.70 mmol) of methyl trifluoromethanesulfonate under nitrogen with stirring for 30 min while the temperature was maintained at −78 °C. The resultant mixture was then stirred overnight at room temperature. Ether (60 mL) was added to the mixture resulting in the slow formation of white crystals. The crystals were collected by filtration and washed three times with ether. The product was purified by recrystallization from methylene chloride and ether at room temperature to give a yield of 2.45 g (88.6%). ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.61 (d, br, J = 8.5 Hz, 1H), 7.58 (d, J = 8.5 Hz, 1H), 7.55 (t, J = 1.7 Hz, 1H), 7.38 (t, br, J = 8.0 Hz, 4H), 7.13−7.20 (m, 3H), 7.09 (d, br, J = 7.5, 4H), 3.19 ppm (s, 6H, CH_3). Anal. Calcd for $C_{21}H_{20}NO_3S_2F_3$: C, 55.37; H, 4.42; N, 3.09. Found: C, 55.26; H, 4.59; N, 3.19.

Preparation of [3-(*N,N*-Diphenyl)amino]phenyl Dimethyl Sulfonium Hexafluorophosphate (7). A fresh 20 mL solution of KPF_6 (1.14 g, 5.98 mmol) in water was added to a solution of [3-(*N,N*-diphenyl)amino]phenyl dimethyl sulfonium trifluoromethanesulfonate **(5)** (1.3 g, 2.86 mmol) in 15 mL of acetone. The mixture was stirred for 2 h at room temperature in the dark. The solid was collected by filtration and redissolved in 10 mL of acetone. The above anion-exchange was repeated three times. The resultant white solid was washed three times with water and ether. The solid was purified by two precipitations from a 10 mL acetone solution through the addition of 50 mL of diethyl ether. The final product yield was 1.08 g (83.6%). ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.62 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.55 (s, 1H), 7.38 (t, br, J = 8.2 Hz, 4H), 7.13−7.20 (m, 3H), 7.09 (d, J = 8.5, 4H), 3.19 ppm (s, 6H, CH_3). Anal. Calcd for $C_{20}H_{20}NSF_6P$: C, 53.22; H, 4.47; N, 3.10. Found: C, 53.20; H, 4.29; N, 3.13.

Preparation of [3-(*N,N*-Diphenyl)amino]phenyl Dimethyl Sulfonium Hexafluoroantimonate (8). A fresh 20 mL portion of $NaSbF_6$ (1.14 g, 4.40 mmol) in water was added to a solution of [3-(*N,N*-diphenyl)amino]phenyl dimethyl sulfonium trifluoromethanesulfonate **(5)** (1.0 g, 2.19 mmol) in 10 mL of acetone. The mixture was stirred for 2 h at room temperature in the dark. The solid was collected by filtration and redissolved in 10 mL of acetone. The above anion-exchange was repeated three times. The resulting white solid was washed three times with water and ether. The product was purified by two precipitations from a 10 mL acetone solution through the addition of 50 mL of diethyl ether. The final product yield was 1.02 g (85.9%).

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^{1}H NMR (500 MHz, d_6-DMSO) δ 7.62 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.55 (s, 1H), 7.38 (t, br, J = 8.2 Hz, 4H), 7.13−7.20 (m, overlap, 3H), 7.09 (d, J = 8.5, 4H), 3.19 ppm (s, 6H, CH$_3$). Anal. Calcd for $C_{20}H_{20}NSF_6Sb$: C, 44.30; H, 3.72; N, 2.58. Found: C, 44.29; H, 3.76; N, 2.54.

Preparation of [3-(*N,N*-Diphenyl)amino]phenyl Benzyl Methyl Sulfonium Hexafluoroantimonate (9). 3-Benzylthiotriphenylamine (1.48 g, 4.03 mmol) was dissolved in 30 mL of dry methylene chloride and cooled to −78 °C in the dark. To this solution was added via syringe 0.46 mL (0.67 g, 4.07 mmol) of methyl trifluoromethanesulfonate under nitrogen. The mixture was then stirred for 30 min while the temperature was maintained at −78 °C. The mixture was then allowed to warm to room temperature and was stirred overnight. Ether (60 mL) was added resulting in the formation of a light green oil. The solvent was decanted and the oil was dried in vacuo at room temperature. The product was used in the ion-metathesis described below without further purification.

A fresh 20 mL portion of aqueous NaSbF$_6$ (2.10 g, 8.11 mmol) was added to a solution of [3-(*N,N*-diphenyl)amino]phenyl benzyl methyl sulfonium trifluoromethane-sulfonate (**6**) (1.3 g, 2.86 mmol) in 10 mL of acetone. The mixture was stirred for 2 h at room temperature in the dark. The solid was collected by filtration and redissolved in 10 mL of acetone. The above anion-exchange was repeated three times. The resultant white solid was washed three times with water and ether. The product was purified by reprecipitation twice from a 10 mL acetone solution by the addition of 50 mL of diethyl ether giving a final yield of 1.08 g (71.8%). ^{1}H NMR (500 MHz, CD$_3$COCD$_3$) δ 7.58−7.62 (m, overlap, 2H), 7.55 (t, J = 7.7 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.7 Hz, 4H), 7.25−7.32 (m, 4H), 7.17 (t, J = 7.7 Hz, 2H), 7.02 (d, J = 8.0, 4H), 5.25 (d, J = 12.5 Hz, 1H, CH$_2$), 5.02 (d, J = 13.0 Hz, 1H, CH$_2$), 3.52 ppm (s, 3H, CH$_3$). Anal. Calcd for $C_{26}H_{24}NSF_6Sb$: C, 50.51; H, 3.91; N, 2.26. Found: C, 50.42; H, 3.98; N, 2.19.

Photolysis of Triphenylamine Sulfonium Salt and Identification of Photoproducts. A 2 mL sample of a 0.05 M solution of **5** in acetonitrile in a glass vessel was purged with nitrogen for 30 min, sealed, and irradiated for 1 h with a 300 nm photochemical lamp. The reaction mixture was poured into 5 mL of water and extracted twice with 10 mL of ether. The combined extract was concentrated to 10 mL under reduced pressure and analyzed by GC-MS. The presence of the H-transfer product 3-methylthio triphenylamine was confirmed by comparison with an authentic sample, and the other coupling products were identified by their mass spectra. The relative product distribution was estimated from the peak areas, neglecting differences in their response factors.

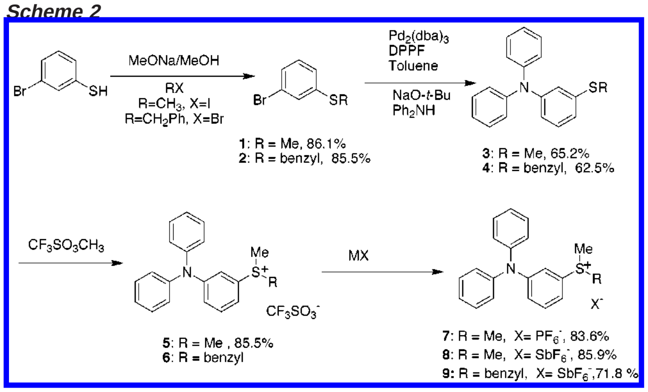
Measurement of Photoacid Generation Quantum Yields. The photoacid generation quantum yields were measured by using Rhodamine B base as an acid indicator,[11] which is protonated by acid produced in the photolysis to give a characteristic absorbance at 555 nm in acetonitrile. The acid concentration in acetonitrile was determined by a calibration curve of rhodamine B titrated with *p*-tolunesulfonic acid in acetonitrile. The monochromated lamp output of the Fluorolog-III fluorimeter was used as the irradiation source. The photon doses at 245 and 294 nm were determined by ferrioxalate actinometry and the uncertainty of the measured dose is ±3%.[12] Acetonitrile solutions of **5**, **7**, **8**, and **9** were irradiated at 294 nm, and solutions of **10** were irradiated at 245 nm. The optical density of the samples was greater than 2.5 at the irradiation wavelength, so all photons incident on the solution could be assumed to be absorbed. The dose rates were kept sufficiently small that the maximum conversion was lower than 15%. The uncertainties in the photoacid generation quantum yields are estimated to be ±10%.

Photopolymerizations. Aliquots (1.0 mL) of a solution containing 3.16×10^{-3} mol/L of either **5**, **7**, **8**, **9**, or **10** and 7.91 mol/L of cyclohexene oxide in methylene chloride were sealed in 4-mL capped vials and irradiated at 300 nm in a merry-go-round holder. After various intervals the sample tubes were withdrawn from the irradiation chamber and any ionic reactions were quenched by the immediate addition of 1 mL of 2 M ammonia in methanol. Methanol was added and the solutions were stirred until the polymers precipitated as powders. The powders were collected by filtration and dried in vacuo for 40 h. The conversion of monomer was determined gravimetrically.

Results and Discussion

Synthesis. Triphenylamines bearing sulfonium groups were prepared from 3-bromothiophenol in four steps (Scheme 2). Alkylation of sodium 3-bromothiophenoxide with alkyl halides in methanol produced 3-bromophenyl alkyl sulfides **1** and **2** in yields of 86.1% and 85.5%, respectively. Pd-catalyzed coupling of bromophenyl alkyl sulfides **1** and **2** with diphenylamine following the method of Buchwald and Hartwig[13] gave triphenylamine sulfide precursors **3** and **4** in yields of 65.2% and 62.5%, respectively. Finally, alkylation of **3** and **4**, with methyl trifluoromethanesulfonate employing a modified version of the method of Saeva,[9] gives triphenylamine sulfonium triflate salts **5** and **6** in yields generally above 80%. For epoxide polymerization, it is known that the most active photoacid generators have nonnucleophilic anions, such as PF$_6^-$, AsF$_6^-$, or SbF$_6^{-2}$. Therefore, we exchanged the triflate anion for PF$_6^-$, AsF$_6^-$, or SbF$_6^-$, by anion-exchange reactions that were driven to completion by repeating the metathesis three times using an excess of either the potassium or sodium salt of the anion.

Scheme 2



Photophysical and Polymerization Studies. To estimate the driving force for photoinduced electron transfer from the triphenylamine group to the sulfonium moiety, we calculated the free energy change (ΔG_{et}) using the Rehm−Weller equation (eq 1).[14] Here, $E_{ox}(D/D^{+\bullet})$ and $E_{red}(A^{-\bullet}/A)$ are the oxidation potential of the electron donor and reduction potential of the electron acceptor, respectively. $E^*(0,0)$ is the energy of the first excited state and $E_{coul.}$ is the Coulombic energy.

$$\Delta G_{et} = E_{ox}(D/D^{+\bullet}) - E_{red}(A^{-\bullet}/A) - E^{*}(0,0) - E_{coul.} \quad (1)$$

The energy of the excited singlet state $E^*(0,0)$ was obtained from the wavelength of intersection of the normalized absorption and emission spectra, and was estimated to be 349 kJ/mol for each sulfonium salt. Each sulfonium salt has one irreversible

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Table 1. Parameters for Free Energy Change of Photoinduced Intramolecular Electron Transfer and the Relative Fluorescence Quantum Yield of Triphenylamine Sulfonium Salts

	E_{ox1},[a] V	E_{ox2},[a] V	E_{red},[a] V	$E^*(0,0)$, kJ/mol	ΔG_{et}, kJ/mol	$\lambda_{max,fl}$, nm	I_{fl}[b]	Φ_{H^+}
5	1.03	1.23	−1.79	349	−77.3	379	0.02	0.48
7	1.02	1.24	−1.72	349	−85.3	376	0.02	0.48
8	1.01	1.22	−1.74	349	−83.6	375	0.02	0.47
9	1.03	1.30		349		376	0.02	0.41

[a] Peak values vs Ag/AgCl (300 mV/s scan rate) at the constant concentration of 10^{-3} mol/L of sulfonium salts with 0.1 N tetrabutylammonium hexafluorophosphonate as electrolyte. [b] The peak intensity of fluorescence (excited at λ_{max}^{abs} 294 nm) relative to triphenylamine (excited at λ_{max}^{abs} 297 nm) under the same conditions.

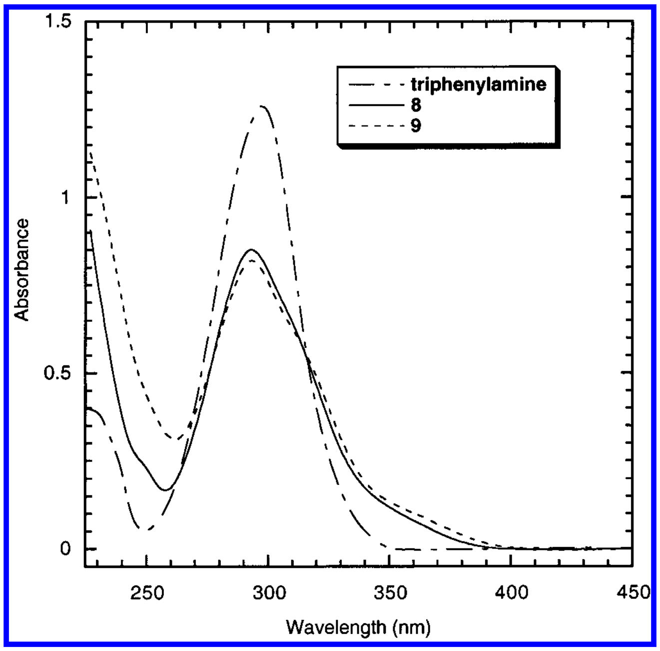

Figure 1. UV−visible absorption spectra of triphenylamine and sulfonium **8** and **9** in acetonitrile. Concentration, 5.0×10^{-5} mol/L.

electrochemical reduction wave and two irreversible oxidation waves. The ΔG_{et} values were calculated by using the Rehm−Weller equation, wherein the peak values of the reduction wave and the first oxidation wave were used to estimate $E_{red}(A^{-\bullet}/A)$ and $E_{ox}(D/D^{+\bullet})$, respectively.[15] The Coulombic energy $E_{coul.}$ was neglected in the calculation. Despite the uncertainty in determining the exact oxidation and reduction potential for the compounds, due to the oxidation and reduction waves being irreversible, the results, shown in Table 1, nonetheless indicate that for these sulfonium salts electron transfer from the aromatic amine to the C−S σ^* orbital is unfavored in the ground state ($\Delta G_{et} > 0$) and that there is a large driving force for electron transfer ($\Delta G_{et} < 0$) from the first excited singlet state.

The positions of the absorption maxima are virtually identical for all the sulfonium salts (Figure 1). It should be noted that the absorption spectra of these sulfonium salts are similar to that of triphenylamine, but have an additional feature on the low energy side. In previous studies on aryl sulfonium ions, a low energy band relative to the aryl $\pi-\pi^*$ band has been assigned to a $\pi-\sigma^*$ transition[5] (Figure 1). Irradiation of the triphenylamine sulfonium salts at 294 nm results in a rapid increase in the fluorescence intensity (which is initially ~2% of that of triphenylamine), and the emission maximum shifts to shorter wavelengths. These data are consistent with decomposition of the sulfonium fragment and formation of fluorescent neutral triarylamines upon irradiation. Analysis of the photolysis products by GC-MS showed that the products consisted of 52% 3-methylthiotriphenylamine (**3**) (identified by comparison with an authentic sample), ~10% of isomers of methyl substituted 3-methylthiotriphenylamine, consistent with previous findings for other photoacid systems, and two products (~18% each) whose molecular mass is consistent with intramolecular coupling of aryl rings to form carbazoles.

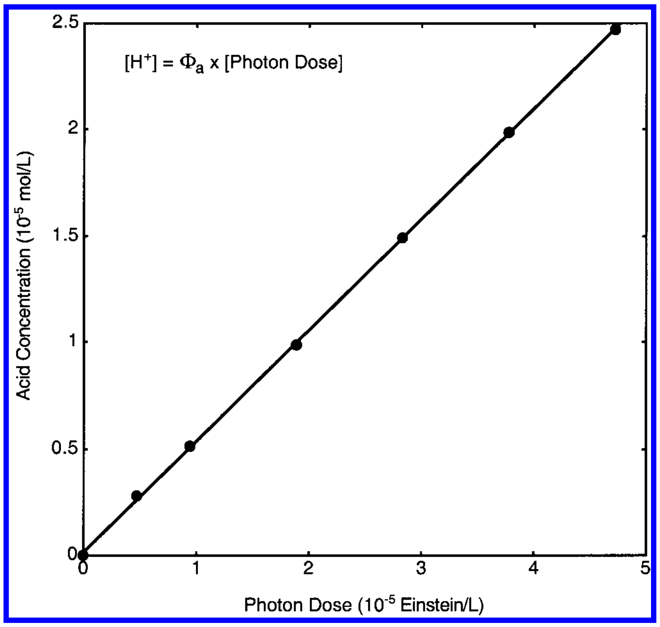

Figure 2. Photoacid concentration of **8** as a function of the absorbed photon dose at 294 nm in acetonitrile. Concentration, 1.5×10^{-4} mol/L; OD_{245} ~2.5; maximum conversion is less than 15%.

The photoacid generation quantum yields were measured by the method reported by Scaiano.[11] For triphenylamine sulfonium salt **8** a plot of the acid concentration versus absorbed photon dose (Einsteins) was linear, and the slope of the line was used to determine the photoacid generation quantum yield (Figure 2). Similarly the quantum yield for triphenylsulfonium salt **10** was measured and the value of 0.50 was obtained. This is in good agreement with the literature value of 0.53.[16] The values of acid generation quantum yields determined in this manner for salts **5**, **7**, **8**, and **9** are 0.48, 0.48, 0.47, and 0.41, respectively. Thus, each one of these salts is an efficient photoacid.

These results are very different from those observed for a simple phenyl dimethyl sulfonium salt, which, as noted above, is not active in photoacid generation, but are consistent with Saeva's observation that the anthracenyl-substituted dimethyl sulfonium salt **11** is an active photoacid.[17] In the case of a simple phenyl dimethyl sulfonium salt, the σ^*orbital (S−C bond) can be populated either by direct $\pi-\sigma^*$excitation or by π^* to σ^* intramolecular electron transfer. The dissociation of the $\pi-\sigma^*$ excited state is energetically unfavorable due to the high total energy of the methyl radical and the phenyl methyl sulfide radical cation species. In contrast, the high acid generation quantum yields of the triphenylamine sulfonium salts reported

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(15) As $E_{ox}^{1/2} < E_{ox}^{p}$ and $E_{red}^{1/2} > E_{red}^{p}$, the real ΔG_{et} value may be more negative than the value calculated from peak potential values.

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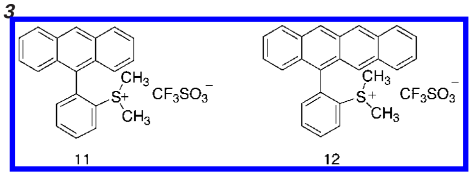
Scheme 3



here show that dissociation is energetically favorable. We suggest that the electron donating ability of the diphenylamine moiety strongly activates the dissociation of the S−C bond by stabilizing the triphenylamine methyl sulfide cation product species, such that the total product energy now favors dissociation from the $\pi-\sigma^*$ excited state.

In the approach used by Saeva, increasing the size of the π-conjugated electron donor apparently provides the energetic stabilization of the radical cation product needed for bond dissociation to be favorable. For example, for compound **11** (Scheme 3), which has a large delocalized chromophore (an anthracenyl group), there is still adequate driving force for excited-state electron transfer from π^* of anthracene to σ^* of the C−S bond ($\Delta G = -19.6$ kJ/mol), as evidenced by a low fluorescence quantum yield of <0.01[17] and a photoacid generation quantum yield of 0.27.[17] However, a further increase in the size of the chromophore results in a lowering of the energy of the π^* state, thus decreasing the driving force for the initial electron-transfer reaction ($\Delta G = 7.5$ kJ/mol). As a result, an analogous naphthacene photoacid, **12**, shows negligible photoacid generation (the photoacid generation quantum yield is 0.003), and this was attributed to a low forward rate of electron transfer that cannot compete with the rate of radiative decay and other nonradiative processes, as evidenced by the relatively high fluorescence quantum yield of 0.47.[17] In the approach that we have employed, substitution of the phenyl group attached to the sulfonium with an electron rich diphenylamine provides both stabilization of the radical cation and a large driving force for electron transfer, as shown in Table 1.

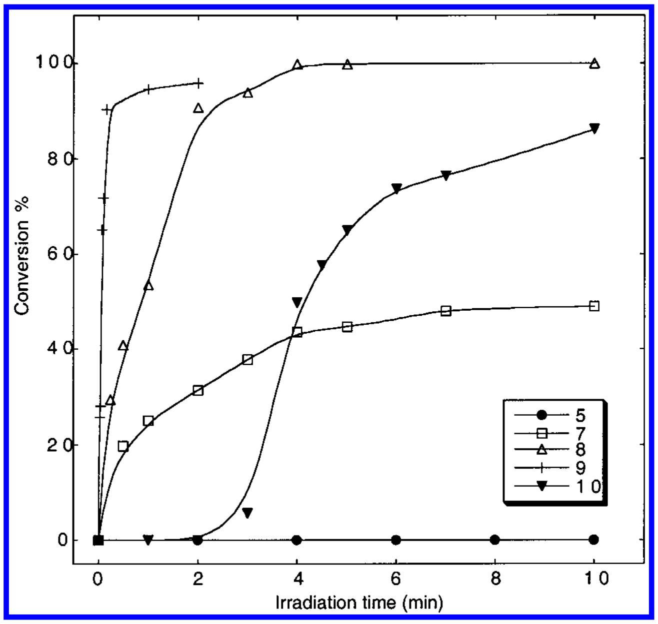


Figure 3. Photopolymerization kinetics of cyclohexene oxide initiated by different triphenylamine sulfonium salts in dichloromethane irradiated at 300 nm. Concentration of monomer, 7.91 mol/L; concentration of initiator, 3.16×10^{-3} mol/L. Lines are a guide to the eye.

Figure 3 shows a comparison of the photopolymerization of cyclohexene oxide with **5**, **7**, **8**, and **9**. In accord with previous observations[2] large anion-dependent variations in the photopolymerization rate were observed. Sulfonium salt **5**, which bears a triflate anion, does not initiate polymerization, even after 1 h of irradiation. In contrast, **8** and **9**, having a SbF_6^- anion, rapidly initiate polymerization, reaching 90% conversion to polymer in 130 s. Although **8** and **9** both have SbF_6^- as the counterion, have similar UV absorption spectra, and have comparable acid generation quantum yields, the polymerization rate of **9** is higher than that of **8**. Park and co-workers suggested that in addition to electron-transfer mediated acid-generation, benzyl-substituted sulfonium salts undergo heterolytic bond cleavage in the excited state to yield a benzylic cation that can itself initiate polymerization efficiently.[18] This could account for why **9** exhibits a higher rate of photopolymerization relative to **8**, as formation of the methyl cation is 316 kJ/mol unfavorable relative to benzyl cation (in the gas phase).[19] Interestingly, **8** and **9** were found to initiate polymerization with extremely short induction times relative to triphenylsulfonium hexafluoroantimonate, when irradiated at 300 nm, under otherwise identical conditions. This demonstrates that triphenylamine sulfonium salts are highly efficient cationic initiators that are sensitive to 300 nm radiation.

Conclusions

These sulfonium salts, bearing nonnucleophilic counterions, form acids very efficiently upon exposure to 300 nm radiation. Stabilization of the radical cation on the sulfur-containing fragment greatly enhances the rate and efficiency of homolytic cleavage of the carbon−sulfur bond. The acids produced in this manner are sufficiently strong to initiate polymerization of epoxides, and thus these sulfonium salts should be useful for photocuring highly viscous media or coatings, as well as for acid-activated material processing and fabrication in the solid phase. Finally, this approach suggests a new design strategy for the synthesis of very efficient photoacids that could be excited over a broad spectral range by either single-photon or multiphoton excitation.[20]

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Supporting Information Available: ^1H NMR spectra of triphenylamine sulfide **3** and **4** and ^1H NMR spectra of triphenylamine sulfonium **5**, **7**, **8** and **9** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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