



Derivatization of  $\beta$ -CD blocks the formation of  $\sigma$ -bonded dimer; presumably this occurs because two derivatized  $\beta$ -CDs with  $\text{TCNQ}^-$  included cannot approach each other closely enough for a  $\sigma$ -bond to form. By use of the Van't Hoff equation and the data from Figure 4, an approximate value for the  $\Delta H$  of reaction (3) was determined to be -100 kJ.

**Acknowledgment.** M.P.E. acknowledges the support of the Office of Organized Research at Northern Arizona University, NSF through the REU program, NIH through its MBRS grant to Northern Arizona University, and Mr. Rick Strattan of Pharmatec, Inc. for a gift of Molecusol. Acknowledgment is made by C.J.H. and M.P.E. to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Mr. Greg Anderson and Mr. David Stewart carried out the thermodynamic studies on the monomer-dimer equilibrium.

## Photo-CIDNP and Nanosecond Laser Flash Photolysis Studies on the Photodecomposition of Triarylsulfonium Salts

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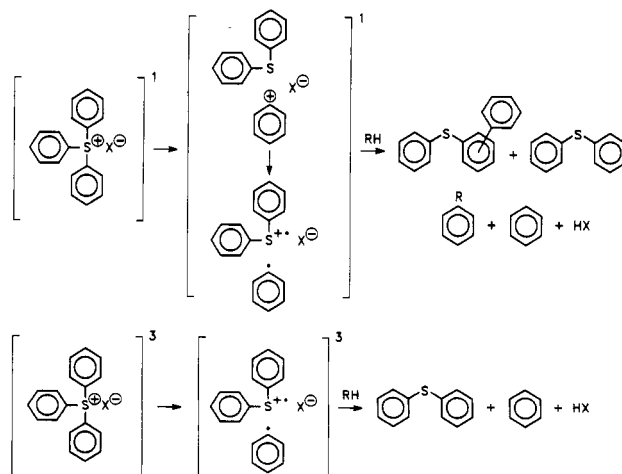
Received March 3, 1992

The direct and sensitized photodecomposition of triarylsulfonium salts have been investigated by nanosecond laser flash photolysis and steady-state photo-CIDNP. The direct photoreaction of triphenylsulfonium salts was shown to proceed via a singlet diphenylsulfanyl radical cation-phenyl radical pair which is produced by internal electron transfer from the initially formed phenyl cation-diphenyl sulfide pair. Recombination of both sets of intermediates gives protonated (phenylthio)biphenyls, identified as a broad transient absorption centered at 465 nm, which lose  $\text{H}^+$  to give 2-, 3-, and 4-(phenylthio)biphenyl. The acetone-sensitized photoreaction gave a triplet excited state of the salt, which then dissociated to give the triplet diphenylsulfanyl radical cation ( $\lambda_{\text{max}}$  750, 340 nm)-phenyl radical pair and subsequently underwent escape reactions with the solvent. Anthracene-, 9,10-diphenylanthracene-, naphthalene-, and perylene-sensitized photoreactions of triphenylsulfonium salts proceeded by electron transfer from the singlet excited state of the aromatic hydrocarbon to give the singlet aromatic hydrocarbon radical cation-triphenylsulfur radical pair, which dissociates to the in-cage triad of diphenyl sulfide, phenyl radical, and the aromatic hydrocarbon radical cation. In the solvent cage naphthalene radical cation can oxidize diphenyl sulfide to diphenylsulfanyl radical cation, identified by transient absorptions at 750 and 340 nm, whereas the other hydrocarbon radical cations cannot. In contrast to the triphenylsulfonium salts, the [(phenylthio)phenyl]diphenylsulfonium salt decomposed via the triplet excited state upon both direct and triplet-sensitized photolysis. Photo-CIDNP gave a strong enhanced absorption which was quenched upon the addition of oxygen and also gave transients, identified as diphenylsulfanyl radical cation ( $\lambda_{\text{max}}$  750, 340 nm), upon both direct and triplet-sensitized photolysis.

### Introduction

In recent years the onium salts of sulfur and iodine have found extensive application as photochemical polymerization initiators.<sup>2</sup> These onium salts have proven to be especially useful as photochemical sources of protic acid, which can then induce polymerization of a wide variety of monomers or defunctionalize acid-sensitive groups attached to polymers. Because of their great importance, a number of studies dealing with the photodecomposition of onium salts have appeared in the literature.<sup>2-9</sup> The

**Scheme I. Photodecomposition Pathways for Triphenylsulfonium Salts from the Singlet and Triplet Excited States**



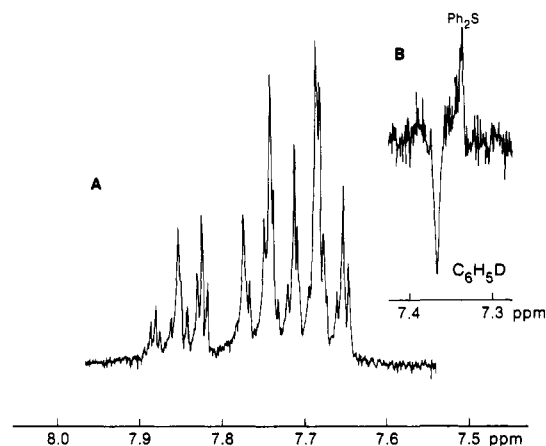
photochemistry of these salts is quite complex due to the fact that both in-cage and cage-escape reaction products

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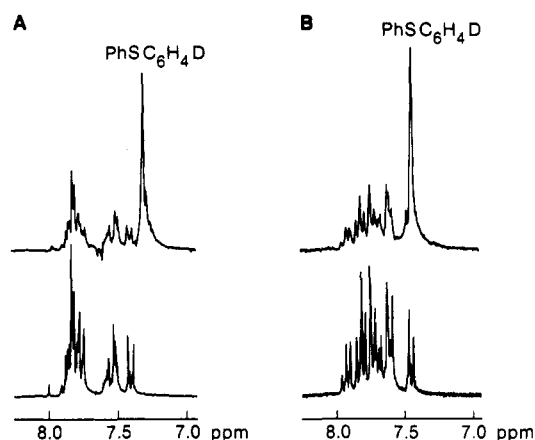
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**Figure 1.** Photo-CIDNP spectra acquired from direct photolysis of TPS-Tf in  $\text{CD}_3\text{CN}$ . (A) Spectrum acquired before photolysis. (B) Inset, a spectrum acquired during photolysis of TPS-Tf. The emission is from benzene- $d_1$  and the upfield band is diphenyl sulfide photoproduct.

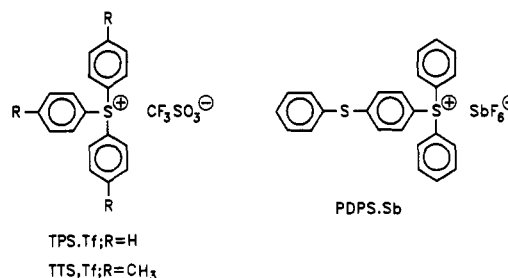
are observed and that evidence has been presented that both heterolytic and homolytic cleavage reaction products can arise from decomposition of the excited state of the onium salt (Scheme I). Triarylsulfonium salts are particularly interesting because it has been proposed that changing to the phenylthio substituent on the aryl ring can divert the photochemistry from the singlet to the triplet manifold upon direct photolysis.<sup>9e</sup>

We report here the results from our steady-state photo-CIDNP (chemically induced dynamic nuclear polarization) and nanosecond laser flash photolysis investigation of the photodecomposition of triarylsulfonium salts. These techniques are complementary in elucidation of the photodecomposition mechanism. The photo-CIDNP studies confirm the detection of radical intermediates and give insight to the multiplicity of the escape radicals, whereas the flash photolysis experiments can identify both radical and cation intermediates with lifetimes from 10 ns to milliseconds. The photochemistry of triphenylsulfonium triflate (TPS-Tf), tris(4-tolyl)sulfonium triflate (TTS-Tf) and [4-(phenylthio)phenyl]diphenylsulfonium hexafluoroantimonate (PDPS-Sb) show that heterolysis and/or



**Figure 2.** Photo-CIDNP spectra acquired from photolysis of PDPS-Sb in (A)  $\text{CD}_3\text{CN}$  (direct) and (B)  $(\text{CD}_3)_2\text{C}=\text{O}$  (triplet sensitized). The top spectra were acquired during photolysis, and both spectra show enhanced absorptions for  $\text{C}_6\text{H}_5\text{SC}_6\text{H}_4\text{D}$ . The lower spectra were recorded before photolysis.

homolysis intermediates can be detected under a variety of conditions. The direct, triplet energy transfer and electron transfer sensitized, photochemistry of these salts is described.



## Results

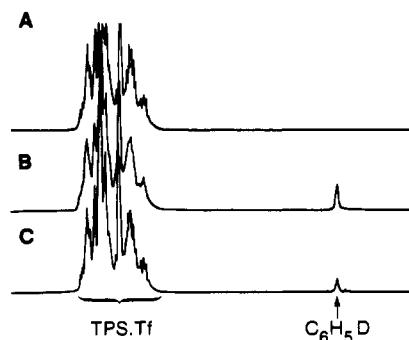
**A. Photo-CIDNP. 1. Direct Photolysis.** The photo-CIDNP spectrum, obtained during the irradiation of the TPS-Tf in  $\text{CD}_3\text{CN}$  at 266 nm, shows only a weak emissive polarization for benzene (Figure 1). The starting material and other products, including diphenyl sulfide and (phenylthio)biphenyl, exhibited no polarizations. Figure 1B shows the benzene emission and diphenyl sulfide photoproduct, the latter signal, with similar intensity, is also detected in the dark spectrum recorded after photolysis. The benzene emission arises from phenyl radical that has escaped from the precursor radical pair and has been subsequently scavenged, presumably by solvent to give benzene- $d_1$ . Applying Kaptein's rules for net polarization, the singlet diphenylsulfinyl radical cation-phenyl radical pair is implicated as the precursor intermediate.<sup>10</sup> The rules for net polarization are summarized in eq 1

$$\Gamma_N = \mu \epsilon \Delta g a_i \quad (1)$$

where  $\Gamma_N$  = the net polarization,  $\mu$  is negative (-) for a singlet radical pair precursor and positive (+) for a triplet radical pair,  $\epsilon$  is positive for geminate (cage) products and negative for scavenging (escape) products,  $\Delta g$  is the sign of  $(g_i - g)$  where  $g_i$  is the  $g$  factor of the radical containing the observed nucleus and  $g$  is the  $g$  factor of the other radical in the pair, and  $a_i$  is the sign of the hyperfine splitting constant for the observed nucleus. Thus, in the case of the direct photolysis of TPS-Tf one expects to

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**Figure 3.** Photo-CIDNP spectra acquired from triplet sensitized photolysis of TPS·Tf in  $(\text{CD}_3)_2\text{C}=\text{O}$ : (A) before photolysis; (B) during photolysis—an enhanced absorption for benzene- $d_1$ ; (C) after photolysis—benzene- $d_1$  photoproduct.

observe a negative polarization for benzene- $d_1$ :  $\mu = \text{singlet} = (-)$ ,  $\epsilon = \text{escape} = (-)$ ,  $\Delta g = (2.0024 - 2.0074) = (-)$ ,  $a_i = 17.4 \text{ G} = (+)$ , and the net polarization is given by eq 2

$$\Gamma_N = (-)(-)(-)(+) = (-) \quad (2)$$

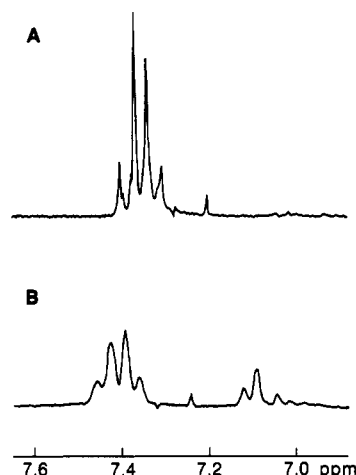
Polarizations arising from the recombination of the radical pair or from other products could not be discerned due to the complex nature of the aromatic region of the starting material spectrum.

The photo-CIDNP spectrum for TTS·Tf on direct photolysis exhibited similar behavior to the TPS salt. A negative net polarization was observed for toluene- $d_1$  which is consistent with a singlet radical pair precursor. The AB quartets for the aromatic protons of both the parent salt and the toluene- $d_1$  product appeared as a broad singlet under these NMR conditions; however, the AB quartet for the escape toluene- $d_1$  can be resolved from indirect photolyses (vide infra).

The photo-CIDNP spectrum recorded during direct photolysis of PDPS·Sb in  $\text{CD}_3\text{CN}$  shows a net enhanced absorption at 7.32 ppm for diphenyl sulfide- $d_1$ , and if the solution was purged with argon prior to photolysis a 3-fold enhancement of this absorption could be obtained (Figure 2A). From Kapstein's rules (eq 1) it is expected that a singlet species should give a negative polarization, however the enhanced absorption for diphenyl sulfide- $d_1$  actually observed during photolysis of PDPS suggests that  $\mu$  is  $(-)$ . Thus the observations that this absorption is partially quenched by oxygen and that it is the opposite polarization from that observed from direct photolysis of TPS·Tf suggest that this species is formed from the escape diphenyl sulfide radical from a triplet radical pair.

**2. Triplet-Sensitized Photoreaction.** The photo-CIDNP spectra for the triplet-sensitized irradiation of TPS·Tf in acetone show an enhanced absorption for benzene, opposite to the polarization obtained from the direct photolytic reaction of TPS·Tf in acetonitrile (Figure 3). This change in polarization from the direct photolysis suggests a change in spin multiplicity for the phenyl radical and indicates that phenyl radical is formed from a triplet phenyl radical-diphenylsulfanyl radical cation pair and has escaped to be scavenged by solvent. Similarly, no significant polarizations were observed for the other species present including the triphenylsulfonium salt.

The photo-CIDNP spectrum of the triplet sensitized decomposition of TTS·Tf shows a net enhanced absorption for toluene- $d_1$  (Figure 4). In this case the AB quartet of the toluene- $d_1$  photoproduct is resolved. The results are consistent with Kapstein's formalism for net polarization. All four peaks of the AB quartet exhibit enhanced absorption, although the low field half of the quartet is more strongly polarized than the high-field portion, due in part



**Figure 4.** Photo-CIDNP spectra acquired from triplet-sensitized photolysis of TTS·Tf in  $(\text{CD}_3)_2\text{C}=\text{O}$ : (A) before photolysis; (B) during photolysis—an enhanced absorption for 4-toluene- $d_1$ .

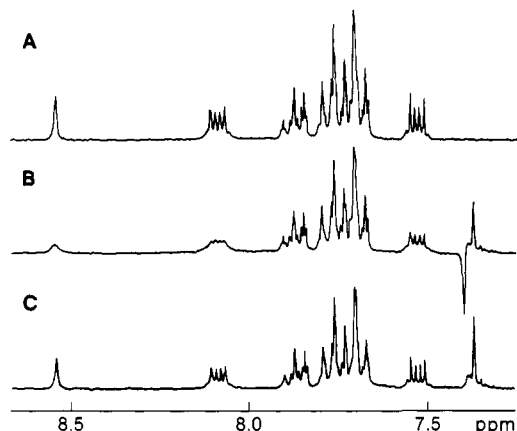
to the multiplet effect.<sup>10</sup> The sign of the pure multiplet effect is predicted by the following relationship:

$$\Gamma_M = \mu \epsilon a_i a_j J_{ij} \sigma_{ij} \quad (3)$$

where  $J_{ij}$  is the coupling constant between nuclei  $i$  and  $j$  and where  $\sigma_{ij}$  is  $(+)$  when nuclei  $i$  and  $j$  are part of the same radical or  $(-)$  when they are parts of different radicals. A positive  $(+)$  multiplet effect exhibits low-field emission and high-field absorption and vice versa for a negative  $(-)$  multiplet effect. For acetone-sensitized photolysis of TTS·Tf:  $\mu = (+)$ ,  $\epsilon = (-)$ ,  $a_i = 17.4 \text{ G} = (+)$ ,  $a_j = 5.9 \text{ G} = (+)$ ,  $J_{ij} = 6 \text{ Hz} = (+)$  and  $\sigma_{ij} = (+)$ . Thus  $\Gamma_M$  is negative, predicting an A/E multiplet, where the low-field signals show an enhanced absorption and the high-field signals show an emission. The photo-CIDNP signals from the triplet-sensitized photolysis of TTS·Tf are not solely due to a pure multiplet effect and thus eq 1, which predicts a net enhanced absorption, also needs to be considered. The observed signals are a combination of the net effect and the multiplet effect, the degree of which is a function of the ratio  $\Delta g H_c : a_H$ . As the magnitude of this ratio decreases a greater degree of multiplet effect polarization is superimposed on the pure net effect spectrum. In this case the ratio for the high-field half is approximately 17 versus 49 for the low-field half.

The photo-CIDNP spectrum recorded during triplet sensitized photolysis of PDPS·Sb in  $(\text{CD}_3)_2\text{C}=\text{O}$  (Figure 3B) also shows a net enhanced absorption at 7.46 ppm for diphenyl sulfide, i.e. triplet and direct photolysis of PDPS·Sb give identical polarizations for the escape radical species.

**3. Photoinduced Electron Transfer.** Photolysis of triphenylsulfonium salts in the presence of aromatic hydrocarbons proceeds by an electron-transfer reaction to give the aromatic hydrocarbon radical cation and triphenylsulfur radical, which rapidly decomposes to diphenyl sulfide and phenyl radical.<sup>5,7b,9d</sup> Photo-CIDNP studies on anthracene-, diphenylanthracene-, perylene-, and naphthalene-sensitized photolysis of triphenylsulfonium triflate show a strong benzene emission and no other polarizations. Figure 5 shows the spectra obtained from anthracene and TPS before, during, and after photolysis. The spectrum obtained during photolysis shows broadening of all the anthracene resonances, an emission at 7.38 ppm from benzene- $d_1$ , and a new absorbance at 7.36 ppm due to formation of a photoproduct which was identified as diphenylsulfide by comparison with an authentic sample. Kapstein's rules predict an emission for benzene- $d_1$  if



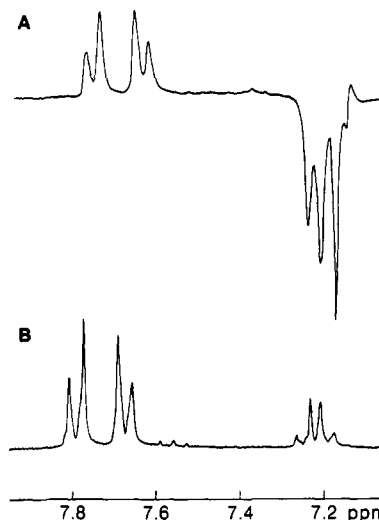
**Figure 5.** Photo-CIDNP spectra acquired from anthracene-sensitized photolysis of TPS·Tf in  $\text{CD}_3\text{CN}$ : (A) before photolysis; (B) during photolysis—an emission for benzene- $d_1$  and upfield diphenyl sulfide photoproduct; (C) after photolysis—benzene- $d_1$  and diphenyl sulfide photoproducts.



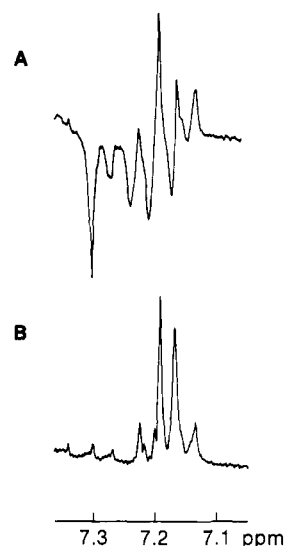
**Figure 6.** Photo-CIDNP spectrum acquired during photolysis of TTS·Tf with 9,10-diphenylanthracene in  $\text{CD}_3\text{CN}$ .

phenyl radical is formed from a singlet precursor and escapes to be scavenged by solvent. Combination of phenyl radical with the aromatic hydrocarbon radical cation to give phenylated arenes, isolated from steady-state photolysis in solution, was not observed by photo-CIDNP.<sup>7,9d</sup> These results agree well with those obtained by DeVoe and co-workers for the perylene-sensitized photodecomposition of triphenylsulfonium hexafluorophosphate.<sup>7</sup>

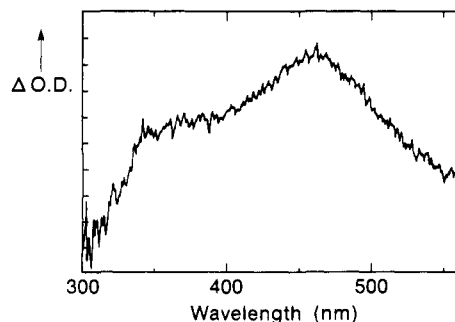
Similar results for the electron transfer sensitized photolysis of TTS·Tf were obtained. As the electron-transfer reaction is from the singlet excited state, the net effect,  $\Gamma_N$ , predicts an emission for toluene- $d_1$ , and the multiplet effect is positive, predicting an E/A multiplet where the low-field signals show an emission and the high-field signals show an enhanced absorption. In these cases, however,  $\Delta g$  is very small (approximately  $-0.0004$ ) leading to  $\Delta gH_o/a_H$  values of 4.0 and 1.3 for the protons ortho and meta to the radical center of the tolyl radical, respectively. As a result, these spectra exhibit less of a net effect and a greater degree of multiplet effect than in the triplet reaction. Thus the three aromatic hydrocarbons exhibit different degrees of the multiplet effect with TTS·Tf. In Figure 6, 9,10-diphenylanthracene shows significant broadening, and toluene- $d_1$ , while broadened, is a net emission during photolysis. In Figure 7, perylene and toluene- $d_1$  are significantly broadened and the three low-field signals of toluene- $d_1$  emit whereas the high-field signal exhibits a zero polarization due to a combination of net effect and multiplet effect.<sup>11</sup> Finally, Figure 8 shows a



**Figure 7.** Photo-CIDNP spectra acquired from photolysis of TTS·Tf with perylene in  $\text{CD}_3\text{CN}$ : (A) during photolysis; (B) after photolysis.



**Figure 8.** Photo-CIDNP spectra acquired from photolysis of TTS·Tf with anthracene in  $\text{CD}_3\text{CN}$ : (A) during photolysis; (B) after photolysis.



**Figure 9.** Absorption spectrum of transient detected from direct photolysis ( $\lambda = 266$  nm) of TPS·Tf in acetonitrile.

different combination of net and multiplet effects for the polarizations of toluene- $d_1$  from photolysis of TTS·Tf with anthracene. In this case low-high-field signals from toluene- $d_1$  at 7.22, 7.19, 7.16 and 7.13 ppm give zero, absorptive, zero, and absorptive polarizations respectively.<sup>11</sup>

**B. Nanosecond Laser Flash Photolysis. 1. Direct Photolysis.** Flash photolysis with excitation at  $\lambda = 266$  or 308 nm of TPS·Tf in acetonitrile gave similar results.

(11) The effects of combining  $\Gamma_N$  and  $\Gamma_M$  are not simply additive. For examples of reactions where polarizations can deviate from those predicted by Kapstein's rules, see: Hutton, R. S.; Roth, H. D.; Bertz, S. H. *J. Am. Chem. Soc.* 1983, 105, 6371.

## Scheme II. Acid Production from Protonated (Phenylthio)biphenyl

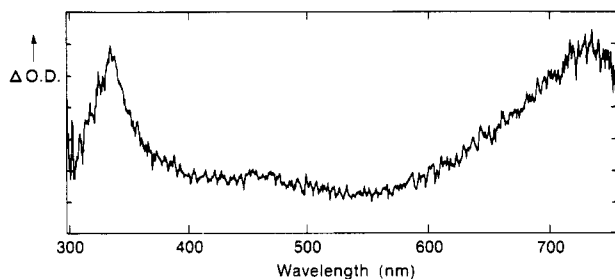
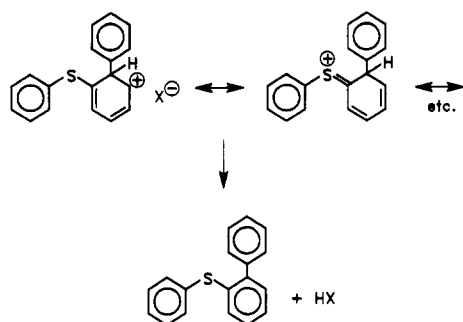


Figure 10. Absorption spectrum of transient detected from triplet-sensitized photolysis ( $\lambda = 308$  nm) of TPS·Tf in acetone.

Figure 9 shows a broad, long-lived transient with  $\lambda_{\max} = 465$  nm. Absorption due to the diphenylsulfanyl radical cation ( $\lambda_{\max} = 750$  nm) was not observed.<sup>5f</sup> The lifetime of the 465-nm transient was solvent dependent. For example the lifetime in acetonitrile was 11  $\mu\text{s}$ , in methanol, 25  $\mu\text{s}$ , and in ethanol, 32  $\mu\text{s}$ . However the lifetime was unaffected by the addition of cumene, a radical scavenger. The stabilization of this intermediate by a polar solvent, its relatively long lifetime and its insensitivity to cumene suggests that the 465-nm transient is cationic and not a radical species. The protonated (phenylthio)biphenyl, an expected species inferred from the established mechanism, is compatible with the 465-nm species (Scheme II).

Flash photolysis (266 nm) of PDPS·Sb does not give the 465-nm species; however, two strong, long-lived absorptions which decayed on the same timescale were detected at  $\lambda = 340$  and 750 nm. The 750-nm transient agrees well with the transient reported for  $\text{Ph}_2\text{S}^{+\cdot}$  observed from the photolysis of diphenyl sulfide in the presence of a phenanthrolium salt.<sup>5f</sup> Thus the observation of  $\text{Ph}_2\text{S}^{+\cdot}$  from direct photolysis of PDPS·Sb also suggests a triplet radical pair as intermediates.<sup>9e</sup> Also the lack of absorptions due to  $\text{Ph}_2\text{S}^{+\cdot}$  from direct photolysis of TPS·Tf indicates that the formation of radicals does not occur, is only a minor process, or that the singlet radical pair recombines faster than the time scale of the experiment.

**2. Triplet-Sensitized Photoreaction.** Flash photolysis (308 nm) for the acetone-sensitized photoreaction of TPS·Tf gave two fairly intense long-lived transient absorptions at 340 and 750 nm (Figure 10). The lifetimes of these absorptions were approximately 20  $\mu\text{s}$  and are assigned to the intermediate diphenylsulfanyl radical cation.<sup>5f</sup> The similarity between photolytic behavior of TPS·Tf upon triplet sensitization and direct photolysis of PDPS·Sb in both photo-CIDNP and nanosecond flash photolysis suggests that both compounds photodecompose along the same triplet manifold.

**3. Photoinduced Electron Transfer.** Flash photolysis of the naphthalene-sensitized photoreaction gave two transient absorptions at 340 and 750 nm with lifetimes of 22–23  $\mu\text{s}$ . Identical absorptions are also detected from

triplet-sensitized photolysis of TPS·Tf and direct photolysis of PDPS·Sb, and all have similar lifetimes. Thus the naphthalene-sensitized reaction also results in formation of diphenylsulfanyl radical cation. The absorption of naphthalene precludes the observation of phenyl radical which absorbs below 300 nm.<sup>12</sup> In contrast, the 340- and 750-nm absorptions were not detected by flash photolysis in the presence of the other electron-transfer sensitizers used in the above photo-CIDNP experiments. The only other transients detected in these experiments were at  $\lambda = 425$  nm, the triplet excited state of anthracene, and at  $\lambda = 410$  nm, the triplet excited state of naphthalene.<sup>13</sup>

## Discussion

Ideally the photo-CIDNP studies should reveal information about the multiplicity of the in-cage and cage-escape radical intermediates. Unfortunately, many radical processes are rendered undetectable by photo-CIDNP due to broadening phenomena.<sup>10</sup> Also nanosecond flash photolysis should detect all the intermediates formed from triarylsulfonium salt photolysis. Again there are limitations due to: (1) weakly absorbing transients; (2) ground-state absorptions by solvent, precursor, or sensitizer; (3) lifetime of the transient, too short or too long; (4) wavelength of the transient absorption, experimentally restricted to 300–800-nm region. However the combined photo-CIDNP and nanosecond flash photolysis studies, along with our earlier photoproduct studies,<sup>9</sup> allow the development of a clearer picture of how triarylsulfonium salts decompose upon direct and sensitized photolysis.

The direct photolysis studies on triphenylsulfonium salts provide evidence for both homolytic and heterolytic cleavage pathways. The photo-CIDNP shows a weak emission for the escape singlet phenyl radical, whereas the nanosecond flash photolysis shows the protonated phenylthiobiphenyl at 465 nm. The absence of the 340- and 750-nm transients due to diphenylsulfanyl radical cation in the flash photolysis experiments upon direct photolysis indicate that either the singlet phenyl radical–diphenylsulfanyl radical recombine at too fast a rate to be observed on this time scale, or that homolysis occurs only to a minor extent. The latter is the more likely explanation because the 340- and 750-nm absorptions are readily detected in both the acetone-(triplet) and the naphthalene-(singlet) sensitized experiments. Also, the photo-CIDNP gives a strong emission for the escape (singlet) phenyl radical in the aromatic hydrocarbon sensitized reactions, and so it is possible to obtain direct evidence for the singlet diphenylsulfanyl radical cation–phenyl radical pair by these techniques. The above results indicate that direct photolysis of TPS·Tf proceeds mainly by heterolysis, and homolysis is a relatively minor process. These results also support the conclusions from our previous work on photoproduct studies of direct photolysis of TPS salts. Phenyl cation was invoked to explain acetanilide and anisole formation in acetonitrile and methanol, respectively, and also to explain the formation of 3-(phenylthio)biphenyl.<sup>9e</sup> Unfortunately, the flash photolysis experiments are unable to directly observe phenyl radical because it has been reported that this species is weakly absorbing with  $\lambda_{\max}$  at 235–245 nm.<sup>12</sup> Phenyl cation is a very reactive transient and likely exists on the picosecond time scale in solution.

(12) (a) Cercek, B.; Konshaug, M. *J. Phys. Chem.* 1970, 74, 4319. (b) Ikeda, N.; Nakashima, N.; Yoshihara, K. *J. Am. Chem. Soc.* 1985, 107, 3381. (c) Hatton, W. G.; Hacker, N. P.; Kasai, P. H. *J. Chem. Soc., Chem. Commun.* 1990, 227.

(13) Charmichael, I.; Hug, G. L. *Handbook of Organic Photochemistry, Volume I*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; p 369.

In contrast to the other sulfonium salts, direct photolysis of PDPS-Sb shows evidence only for homolytic cleavage from the excited state. The transient which absorbs at 340 and 750 nm is readily detected and agrees well with the 750-nm transient previously reported for diphenylsulfinyl radical cation.<sup>5d</sup> In addition the 465-nm transient, due to a protonated (phenylthio)biphenyl, is not observed. The photo-CIDNP experiments also show an enhanced absorption for diphenyl sulfide from direct photolysis of PDPS-Sb, implicating an escape reaction from a triplet radical pair. Similarly triplet sensitization of this salt in acetone shows the identical behavior in the photo-CIDNP and flash photolysis experiments. Thus it is concluded that direct and triplet-sensitized photolysis of PDPS-Sb proceeds by homolysis from the triplet manifold to give the diphenylsulfinyl radical cation–diphenyl sulfide radical pair. This also agrees well with photoproduct studies on PDPS-Sb where no in-cage products were detected, and it was proposed the only detectable product, diphenyl sulfide, was formed by homolysis from the triplet excited state.<sup>9e</sup>

In contrast to the direct photoreaction, triplet-sensitized photolysis of TPS-Tf gives the 340- and 750-nm transients for diphenylsulfinyl radical cation and shows an enhanced absorption for benzene. These data confirm both the homolytic cleavage reaction and the intermediacy of triplet radical pair. Again the photoproduct studies of triplet-sensitized reactions support homolysis of the triplet excited state to give a triplet radical pair. Triplet-sensitized photolysis of TPS salts gives no (phenylthio)biphenyls or acetanilide in acetonitrile, indicating an escape reaction where phenyl cation is not an intermediate.<sup>9e</sup> The only photoproducts were diphenyl sulfide and benzene, which are formed from the triplet diphenylsulfinyl radical cation–phenyl radical pair.

The photo-CIDNP studies on the electron-transfer reactions between TPS-Tf and aromatic hydrocarbons show an emission for the escape phenyl radical reacting with solvent and line broadening for the hydrocarbon radical cation. This observed emission confirms the singlet nature of the electron-transfer reaction. Electron transfer and energy transfer are both energetically unfavorable from the triplet excited states of the aromatic hydrocarbons studied.

The interesting case for the photoinduced electron transfer reactions is naphthalene. The initially formed in-cage intermediates, naphthalene radical cation, triphenylsulfur radical, and anion, rapidly decompose to the tetrad of naphthalene radical cation, diphenyl sulfide, phenyl radical, and anion. Combination of the radicals give phenyl-naphthalenes, diphenyl sulfide and Bronsted acid, whereas in-cage electron transfer gives naphthalene, diphenylsulfinyl radical cation, phenyl radical, and anion. Diphenyl sulfide ( $E_{ox} = 1.31$  V)<sup>14</sup> can be oxidized by the radical cation of naphthalene ( $E_{ox} = 1.54$  V),<sup>15</sup> whereas the radical cations of the other aromatic hydrocarbons (anthracene,  $E_{ox} = 1.09$  V;<sup>16</sup> diphenylanthracene,  $E_{ox} = 0.92$  V;<sup>16</sup> perylene,  $E_{ox} = 0.85$  V<sup>16</sup>) cannot oxidize diphenyl

sulfide. The photo-CIDNP, nanosecond flash photolysis, and photoproduct studies all lend evidence to this sequence of events. The photo-CIDNP shows an emission for the escape (singlet) phenyl radical reacting with solvent, the flash photolysis experiments detect the 340- and 750-nm transients for diphenylsulfinyl radical cation, and the 2- and 4-(phenylthio)biphenyls are major photoproducts from photolysis in the presence of naphthalene. In contrast, while an emission for the escape phenyl radical reaction with solvent is detected, neither the 340- and 750-nm transient nor the (phenylthio)biphenyl isomers are detected from the photolyses in the presence of anthracene, 9,10-diphenylanthracene, or perylene.

### Conclusions

The photo-CIDNP and flash photolysis results are consistent with a mainly heterolytic cleavage reaction from direct photolysis of triphenylsulfonium salts, whereas triplet-sensitized photolysis with acetone gives the triplet diphenylsulfinyl radical cation–phenyl radical pair, and photoinduced electron-transfer reactions with naphthalene gives the singlet diphenylsulfinyl radical cation–phenyl radical pair. The latter radical pair is not observed in sensitized reactions with the other aromatic hydrocarbons studied because their radical cations cannot oxidize diphenyl sulfide to diphenylsulfinyl radical cation. The direct and triplet-sensitized photolysis the phenylthio-substituted triphenylsulfonium salt decomposes by homolytic cleavage from the triplet excited state to give the triplet diphenylsulfinyl radical cation–phenyl radical pair.

### Experimental Section

Unless stated otherwise, all reactions were carried out in an atmosphere of dry nitrogen or argon. Solvents were dried using standard techniques, and glassware was baked at 120 °C prior to use. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AF-250 spectrometer. All spectra were recorded at ambient temperature, and chemical shifts are reported relative to tetramethylsilane internal standard. Deuterated solvents for the NMR studies were obtained from Aldrich Chemical Co. The synthesis of the sulfonium salts has been described previously.<sup>9e</sup>

**Photo-CIDNP Experiments.** Samples of sulfonium salt [(2-4) × 10<sup>-2</sup> M] in a suitable deuterated solvent were deoxygenated by purging with argon for 5 min and irradiated in the probe of the NMR spectrometer. The irradiation source was an ICL Technologies 300-W high-pressure Xenon pulse lamp equipped with a water filter and was guided to the sample through a Suprasil light pipe. A pulse angle of 15° was employed to minimize distortion of the expected multiplet effects. The number of scans was typically chosen to produce satisfactory signal to noise ratios. The acquisition time was about 5 s per pulse and the relaxation delay was 0.5 s. The total acquisition time was 100–500 s depending on the number of scans.

**Nanosecond Laser Flash Photolysis.** The apparatus was described previously.<sup>17</sup> The sample concentration was adjusted to an optical density of 0.3 at the photolysis wavelength. The sample was degassed with a steady stream of argon. A pulsed Nd:YAG laser frequency doubled or quadrupled was used for 355- and 266-nm photolyses, whereas a XeCl excimer laser was used for 308 nm.

**Acknowledgment.** The Authors at Columbia University thank the NSF and AFOSR for support of this research.

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