The minor product (<5% of the benzene yield) in the phenyl *tert*-amyl reaction mixtures eluted from AGN before any olefin. The product was examined on a vpc–mass spectrum tandem arrangement with a DND column. Mass spectra were recorded at several different points as the gc peak increased and decreased in intensity. The differences in intensities between different spectra at each value of m/e cancel the background and give an indication of the relative intensities of the peaks to be attributed to material being eluted. The latter values were then normalized in the usual way. A strong parent peak appears at m/e 72 and the fragmentation pattern is consistent with the published spectra of isopentane.[12] Excluding heteroatoms, the parent peak at m/e 72 requires C_5H_{12}, namely, *n*-pentane, isopentane, and neopentane. Pentane, isopentane, and the product all have a base peak at m/e 43 ($C_3H_7^+$), whereas neopentane has a base peak at m/e 57 and only a very small peak (1.7%) at m/e 43.[12] *n*-Pentane and isopentane are readily separable on DND and DMS and isopentane coinjects with the product peak on both of these columns.

The benzene collected from the reaction of PAT with each individual sulfide gave mass spectra characteristic of benzene by comparison with that of authentic benzene.

Benzene and chlorobenzene from a reaction mixture of PAT, carbon tetrachloride, and di-*tert*-butyl sulfide were collected by gc from a 0.25 in. di-*n*-decyl phthalate column; mass spectra and retention times agreed with those of authentic material.

Quantitative Analysis of Reaction Products. The olefins and benzene from the reactions of the phenyl amyl sulfides and *tert*-butyl sulfides were measured quantitatively on a 20 ft × $^1/_8$ in., 20% di-*n*-decyl phthalate column on an F & M Model 700 gas chromatograph equipped with a flame detector. Cyclopentane was used as an internal standard. Triplicate injections were made for each sample. Peak areas were measured by planimeter or triangulation.

Standards solutions of the products in the appropriate sulfide were generally prepared along with each set of reaction tubes and response factors determined. However, this was not always the case; since the response factors were reasonably consistent from run to run, an average value for each product was calculated from all the values obtained, and this value was used for each reaction tube.

Since some samples of sulfide contained small amounts of product olefins, corrections were sometimes necessary. A blank tube (1.0 ml of sulfide, degassed and heated with reaction tubes) was doped with a known amount of cyclopentane and analyzed to determine correction factors.

The benzene and chlorobenzene produced by the decomposition of PAT in *tert*-butyl sulfide–carbon tetrachloride mixtures were measured on a $^1/_8$ in. × 1 m, 10% di-*n*-propyl tetrachlorophthalate column in tandem with a $^1/_8$ in. × 2 m, 20% β,β'-oxydipropionitrile column at 70°. *tert*-Butylbenzene was used as an internal standard. Response factors were calculated from the gc analysis of solutions of known composition.

Effect of Added Olefin on Product Yields in the Decomposition of PAT in Phenyl *tert*-Amyl Sulfide. A control experiment was run to verify the assumption that the olefins formed in the elimination reaction are not consumed by subsequent secondary reactions. Two stock solutions were prepared. One was a solution of PAT (0.05 *M*) in phenyl *tert*-amyl sulfide. The other was prepared by adding small amounts of 2-methylbutene-1 and 2-methylbutene-2 *via* microliter syringe to a sample of phenyl *tert*-amyl sulfide to give a solution which was approximately the same in respective olefin concentrations as the phenyl *tert*-amyl sulfide–PAT solutions after decomposition.

Five reaction tubes were then prepared. Each of the first two contained a 1-ml aliquot of the PAT solution. Each of the second two contained a 1-ml aliquot of the PAT solution and a 1-ml aliquot of the olefin solution. The fifth tube contained a 1-ml aliquot of the olefin solution. The tubes were degassed, sealed, and heated in a refluxing ethyl acetate bath, opened, and analyzed by gc. The analyses are presented in Table VI. Averaged values are reported.

Table VI. Stability of Product Olefins to the Reaction Conditions

	Mol × 10^6/tube	
Sample	$CH_2{=}C(CH_3)C_2H_5$	$(CH_3)_2C{=}CHCH_3$
PAT[a]	5.60	12.75
Olefin[b]	4.69	12.95
PAT + olefin[c]	10.63	26.15

[a] PAT in phenyl *tert*-amyl sulfide. [b] Olefin in the sulfide. [c] Olefin + PAT in the sulfide.

The total yield of olefins in the tube containing PAT + olefin in the sulfide should equal the sum of the olefins in the "PAT tube" and the "olefin tube," if the olefins are stable to the reaction conditions. The results show this to be the case; replicate experiments gave comparable results.

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Photolysis of a Charge Transfer Complex. Triphenylsulfonium Iodide

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Abstract: A charge transfer absorption is identified for triphenylsulfonium iodide in chloroform. Selective irradiation of the complex at the wavelength of the CT transition gives stoichiometric conversion of the sulfonium salt to diphenyl sulfide with a quantum yield of 0.35. The phenyl group lost is quantitatively accounted for as iodobenzene and benzene. Triodide ion is also formed. The ratio iodobenzene/diphenyl sulfide is about 0.6 and is not significantly dependent on conversion from 0.05 to 70% reaction. Accordingly, the formation of phenyl products is rationalized by nondiffusive (C_6H_5I) and diffusive (C_6H_6) pathways.

The role of excited charge transfer (CT) complexes in photochemical processes is receiving increasing recognition. These excited states can be formed by irradiation of ground state CT complexes in the CT absorption band or, possibly, by interaction of an excited state with a ground state molecule. Excited CT complexes show a wide range of chemical behavior. For example, irradiation of the CT band of the ben-

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(1) From the Ph.D. Thesis of S. L. N., University of Rochester, 1970.

zene–maleic anhydride complex gives a photoadduct.[2] Pyromellitic dianhydride radical anion is observed as an electron-transfer product from the triplet of the mesitylene–pyromellitic dianhydride complex.[3] Excitation of the CT band of 1-ethyl-4-carbomethoxypyridinium iodide also gives the electron transfer product, 1-ethyl-4-carbomethoxypyridinyl radical.[4] The formation of complexes in the quenching of excited states is firmly established by the work of Weller[5] and seems to be an important mechanism for energy transfer. Emission,[6] electron transfer,[6] intersystem crossing,[6] and rearrangement of the quencher[7] represent some of the possible fates of the excited complex. These complexes have been described in CT terms,[5] although other formations are possible.[8]

The photodecomposition of a variety of onium salts, *e.g.*, $\mathrm{ArN^+Me_3X^-}$,[9] $\mathrm{Ar_3S^+X^-}$,[10] $\mathrm{Ar_2I^+X^-}$,[11] and $\mathrm{Ar_3P^+\text{-}RX^-}$,[12] is known. Several authors[9,10b,c,12b] have suggested a photochemical role for the corresponding CT complexes but have neither identified the complexes nor studied the consequences of selective irradiation of the CT band. A CT absorption is reported for diaryliodonium iodides.[11c]

This paper reports a study of the behavior of triphenylsulfonium iodide (**1**). A CT complex is identified in chloroform; the consequences of selective irradiation of the CT absorption band of this complex are described in detail.

Spectroscopic Observations. The signal characteristic of a CT complex is a new absorption band which cannot be attributed to either of the separate components of the complex.[13] When the donor–acceptor partners are ions, the concentration of the complex, and hence the spectral behavior, will depend on the extent of ion pairing.[13] The ultraviolet spectra of triphenylsulfonium iodide in methanol (Z = 83.61 kcal/mol[14]) and in chloroform (Z = 63 kcal/mol[14]) are dramatically different (Figure 1). The long-wavelength absorption of triphenylsulfonium iodide in chloroform is attributed to a CT transition. Several alternative rationalizations of the origin of the new absorption in chloroform were considered and rejected.

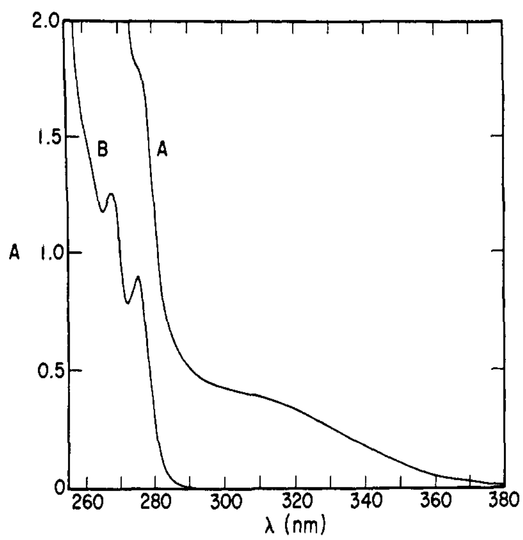

Figure 1. Ultraviolet spectra of triphenylsulfonium iodide (**1**): (A) 3.18 × 10^{-4} M **1** in chloroform, (B) 3.28 × 10^{-4} M **1** in methanol.

(a) Formation of a light-absorbing decomposition product. Dilution of a stock solution of triphenylsulfonium iodide in chloroform (Figure 1, curve A) with successive portions of methanol progressively changes the absorption spectrum until the "methanol spectrum" (Figure 1, curve B) is obtained. Successive dilution of a methanol stock solution with chloroform gives the opposite change. The spectral changes as a function solvent are, therefore, reversible and cannot be attributed to the formation of a decomposition product.

(b) Solvent effects on the absorption spectrum of either component ion. The ultraviolet spectrum of triphenylsulfonium perchlorate is essentially the same in methanol and chloroform and is also identical with the spectrum of the iodide **1** in methanol. These spectra are all attributed to the cation and indicate that there is no appreciable effect of the solvent change from methanol to chloroform on the absorption spectrum of the cation. Iodide ion absorbs at short wavelengths (<300 nm) in a variety of solvents[15] and cannot account for the absorption of triphenylsulfonium iodide in chloroform (>300 nm).

(c) Proximity effects. It is reasonable that the sulfonium cation and the counterion are more closely associated in chloroform than in methanol. One might consider, therefore, the possibility of spectral perturbations due to proximity effects. Such phenomena are known.[15b,16] Proximity effects are not important for the sulfonium perchlorate, since there is no apparent change in the spectrum with a solvent change from methanol to chloroform. Furthermore, previous observations of cation–anion perturbations show a shift in the absorption to shorter wavelengths with increasing proximity of the ions.[15b,16] Triphenylsulfonium iodide shows the opposite effect and pertur-

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bations of the spectrum of either ion by the electronstatic field of the other are, therefore, ruled out.

The preceding arguments contradict several possible explanations of the absorption spectrum of the sulfonium iodide in chloroform; formation of a CT complex remains a reasonable postulate. In particular, we consider the difference in the absorption spectrum of triphenylsulfonium iodide (**1**) in methanol and chloroform to reflect a change in the relative concentrations of dissociated and associated triphenylsulfonium and

$$(C_6H_5)_3S^+ + I^- \rightleftharpoons \underset{\mathbf{1}}{[(C_6H_5)_3S^+I^-]_{CT}}$$

iodide ions. The spectrum observed in methanol is that of the solvated triphenylsulfonium ion, while the new absorption in chloroform is due to a CT transition characteristic of the sulfonium iodide ion pair. Concentration studies (see Experimental Section) support this view. The iodide **1** obeys Beer's law in methanol in the range 6×10^{-4}–4×10^{-2} *M*. At molarities greater than 4×10^{-2}, however, the apparent molar extinction coefficient (based on initial salt concentration) at 305 nm increases with concentration, revealing an increasing fraction of ion pairing. Addition of potassium iodide to a concentrated solution of the sulfonium iodide **1** in methanol gives a similar increase in the apparent extinction coefficient with increasing concentration of iodide ion. The sulfonium iodide in chloroform fails to obey Beer's law in the range 1×10^{-3}–6×10^{-2} *M*. In this case, the apparent extinction coefficient decreases with increasing concentration, reflecting the opposing effects of concentration and ionic strength on the fraction of ions paired. Similar effects are observed for 1-ethyl-4-carbomethoxypyridinium iodide in chloroform.[14] Finally, the sulfonium perchlorate in chloroform follows Beer's law over approximately the same range of concentrations where the iodide **1** deviates. Presumably, a similar change in the fraction of paired ions occurs but is of no spectroscopic significance since the perchlorate ion does not form a charge transfer complex.[17]

The related triphenyloxonium salts were studied briefly to elucidate the role of the sulfur atom in the triphenylsulfonium iodide CT complex. The oxonium fluoroborate shows identical spectra in methanol and chloroform. The oxonium iodide, however, exhibits the same pattern of increased intensity and anomalous long-wavelength absorption in chloroform observed for the sulfonium iodide, suggesting the formation of a similar CT complex.

In summary, the preceding data establish a CT complex of triphenylsulfonium iodide in chloroform. Trivial explanations are ruled out, the effects are specific for iodide ion, and the concentration studies give evidence for an equilibrium between solvated and complexed sulfonium ions. Unfortunately, the CT and the sulfonium cation absorptions overlap and a maximum for the CT transition cannot be assigned with confidence. The behavior of the oxonium ion indicates that the sulfur atom is not uniquely required for CT complex formation.

Photolysis of the CT Complex. The triphenylsulfonium iodide CT complex in chloroform was selectively excited in the CT transition using filtered light ($\lambda > 320$ nm) from a medium-pressure mercury lamp. Benzene, iodobenzene, and diphenyl sulfide are the only important organic photoproducts. Triiodide ion is also formed. Neither chlorobenzene nor biphenyl is observed (0.5% yields would have been detected). The concentration of sulfonium salt remaining was determined from the optical density of the complex formed from the sulfonium cation and cobalt thiocyanate.[18] Benzene, iodobenzene, and diphenyl sulfide were determined gas chromatographically; the sulfonium iodide pyrolyzes to some of these same products[19] and was, therefore, carefully removed from samples before gc analysis. Control experiments involving known concentrations of sulfonium iodide, benzene, iodobenzene, and diphenyl sulfide guaranteed the quantitative aspects of the work-up procedure.

$$[(C_6H_5)_3S^+I^-]_{CT} \xrightarrow[CHCl_3]{h\nu} (C_6H_5)_2S + C_6H_6 + C_6H_5I + I_3^-$$

One mole of diphenyl sulfide is formed for each mol of triphenylsulfonium salt destroyed. The other aromatic ring is quantitatively distributed between benzene and iodobenzene. A typical time study is shown in Table I.

Table I. Photolysis of Triphenylsulfonium Iodide (**1**) in Chloroform

Time, hr	% destruction of I	% yield[a]			$C_6H_5I/(C_6H_5)_2S$
		C_6H_6	C_6H_5I	$(C_6H_5)_2S$	
1	29	11	20	29	0.69
2	43	15	25	41	0.61
3	50	16	30	47	0.64
4	56	17	33	52	0.64
6	65	20	41	64	0.64
9	72	22	45	72	0.63

[a] Based on the initial concentration of **1** (5.0×10^{-2} *M*).

The photolysis rate deviates markedly from zero-order behavior. As illustrated in Table I, conversions during the first, second, and third hours of photolysis were 29, 12, and 6%, respectively. Destruction of the sulfonium salt is not responsible for this behavior; after 72% conversion (9 hr), the remaining sulfonium salt is still sufficient to absorb >99% of the incident light. Rather, the formation of a light-absorbing product, triiodide ion, is indicated. The ultraviolet spectrum of the reaction mixture after photolysis shows the characteristic transitions[20] of triiodide ion at 360 and 290 nm; the ratio of the intensities is in agreement with that reported.[20] Since triphenylsulfonium iodide and triiodide ion have molar extinction coefficients of 200 and 21,600 at 360 nm, respectively, triiodide ion competes for the incident light and causes the decrease in the rate of photolysis of the sulfonium iodide. The chemical consequences of the formation of triiodide ion were studied by artificially generating triiodide ion by the addition of less than stoichiometric amounts of iodine to chloroform solutions of the

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sulfonium iodide prior to photolysis.[21] Solutions of sulfonium iodide, with and without added iodine, were photolyzed simultaneously. The results in Table II show that the per cent photodestruction of sulfonium iodide decreases as the triiodide concentration increases. The experiments at high concentrations of triiodide further demonstrate that the photolysis of triphenylsulfonium triiodide is unimportant and cannot account for the products described in Table I.

Table II. Photolysis of Triphenylsulfonium Iodide–Triiodide Mixtures

	Initial concn, *M*		% yield			$C_6H_5I/$
	$\mathbf{1} \times 10^2$	$I_2 \times 10^2$	$(C_6H_5)_2S$	C_6H_6	C_6H_5I	$(C_6H_5)_2S$
A[a]	4.9	0	20	7.4	13	0.62
	5.1	0.022	19	7.2	12	0.62
	5.2	0.22	13	4.9	8.2	0.63
	5.0	2.2	1.3		1.0	0.82
B[a]	4.7	0	15	6.0	9.7	0.63
	4.7	4.4	0.14		0.096	0.71

[a] Series A and B correspond to different photolysis times and cannot, therefore, be directly compared.

The stoichiometry of the photolysis of triphenylsulfonium iodide was found to be essentially constant over a wide range of conversions (Table III). These observations rule out any important contribution from secondary photolysis of products under our experimental conditions. A solution of benzene, iodobenzene, and diphenyl sulfide at concentrations comparable to those attained at high conversion has an absorbance less than 0.05 at λ >320 nm, leading to the same conclusion. The data in Table III also reveal that the ratio of yields of iodobenzene to diphenyl sulfide shows, at best, a minor trend with per cent conversion. Similar data are included in Tables I, II, and IV.

Table III. Photolysis of Triphenylsulfonium Iodide (**1**)[a] to Varying Conversions

% yield			$C_6H_5I/$
$(C_6H_5)_2S$	C_6H_5I	C_6H_6	$(C_6H_5)_2S$
72	45	22	0.63
58	37	17	0.64
47	30	16	0.63
29	17	11	0.59
15	10	6.0	0.67
5.9	3.4	2.4	0.58
1.0	0.58	0.35	0.58
0.29	0.18	0.13	0.62
0.21	0.21	0.068	0.57

[a] [**1**] ~ 5 × 10^{-2} *M* in chloroform.

Quantum yields for the decomposition of triphenylsulfonium iodide (and, therefore, for the formation of diphenyl sulfide) are shown in Table IV. The possibility of competitive light absorption by triiodide ion dictated photolysis to very low conversions. Each photolysis tube was controlled by a dark tube to detect traces of photolysis during sample preparation and handling. The data show the quantum yields to be essentially independent of conversion in the range studied, indicating that competitive light absorption by triiodide ion is not important under these conditions.

Table IV. Quantum Yields for the Photolysis of Triphenylsulfonium Iodide in Chloroform[a]

Run[b]	Time, min	Φ	% yield $(C_6H_5)_2S$	C_6H_5I	$C_6H_5I/(C_6H_5)_2S$
A	1	0.38	0.053	0.034	0.64
A	4	0.33	0.19	0.13	0.68
B	2	0.36	0.024		
B	4	0.37	0.051	0.031	0.61
B	8	0.34	0.092	0.056	0.61
		$\Phi_{av} = 0.35 \pm 0.009$ (4 deg of freedom)			

[a] [**1**] ~ 0.1 *M*. [b] The dark tube (A) showed less than 0.005% conversion to diphenyl sulfide; run B, less than 0.001% conversion.

Discussion

The preceding data clearly establish a role for an excited charge transfer complex in the photolysis of triphenylsulfonium iodide in chloroform. Thus, selective irradiation of the CT transition gives moderately efficient photodecomposition to diphenyl sulfide, $\Phi = 0.35$. The stoichiometry is straightforward; 1 mol of sulfide is formed for each mol of sulfonium iodide destroyed. By implication, similar excited CT complexes may be involved in the photochemistry of other "onium" salts. It is important to note, however, that other pathways may operate as well. Thus, a variety of "onium" salts which cannot form CT complexes (*e.g.*, BF_4^- salts) are, nevertheless, photolabile.[10a,d,12b] Such results suggest a photochemical role for the cations; the distinction in this paper between dissociated and associated ions should permit a detailed study of the consequences of excitation of the solvated triphenylsulfonium ion. The importance of excited CT complexes in any given system will depend on the characteristics of the ions involved, solvent, concentration, and wavelength. As discussed below, excited CT complexes may also be involved in situations where there is no direct excitation of the ground state complexes.

The fate of the phenyl group that is lost in the conversion of triphenylsulfonium iodide to diphenyl sulfide is interesting. The sum of the yields of benzene and iodobenzene quantitatively accounts for all of these phenyl groups. The formation of benzene implicates a phenyl radical intermediate which abstracts hydrogen from chloroform.[22] It is tempting to account for iodobenzene by a competitive reaction of phenyl radicals with triiodide ion. The data, however, rule out this simple explanation. As shown in the tables, the ratio $C_6H_5I/(C_6H_5)_2S$ is essentially constant (~0.6) over a range of conversions from 0.05 to 70%. The triiodide concentration would be expected to vary over this range of conversions and, therefore, the fraction of phenyl groups diverted to iodobenzene should vary also. The analysis is not completely straightforward, however. High concentrations of triiodide ion are not necessarily formed as the photolysis proceeds, since the pathway producing an iodine atom also gen-

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(21) The equilibrium constant for the formation of triiodide ion in methanol is 10^5 M^{-1}: S. Cormeau and M. Manvebach, *Bull. Soc. Chim. Fr.*, 2576 (1966).

(22) Phenyl cation reacts with methylene chloride to give chlorobenzene and essentially no benzene: J. E. Sheats, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1965. Chlorobenzene was not detected in the photolysis of I in chloroform (0.5% yield would have been observed).

erates an iodine scavenger (·CCl_3).[23] To further probe

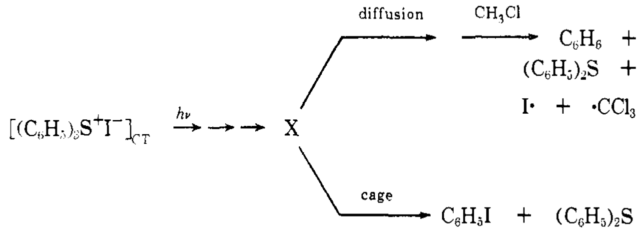
$$[(C_6H_5)_3S^+I^-]_{CT} \xrightarrow{h\nu} \longrightarrow \longrightarrow C_6H_5\cdot + I\cdot$$

$$C_6H_5\cdot + CHCl_3 \longrightarrow C_6H_6 + \cdot CCl_3$$

the role of triiodide ion, phenyl radicals were generated thermally in chloroform containing ~5 × 10^{-2} *M* triiodide ion. Analysis for the relative yields of products established that the phenyl radical partitioned $C_6H_6/C_6H_5I = {}^{44}/_{56}$ at this concentration of triiodide. If the same competition applies to the photodecomposition of triphenylsulfonium iodide, then the C_6H_6/C_6H_5I can be predicted at various concentrations. For example, assuming that 2 mol of sulfonium iodide is destroyed to give 1 mol of triiodide, then a *maximum* of 5 × 10^{-4} *M* triiodide results from 2% decomposition of 5 × 10^{-2} *M* sulfonium iodide. Using the competition ratio from the thermal experiment, one predicts an overwhelming preference for formation of benzene at low conversions. The experiments, however, show that iodobenzene is always the major phenyl product and clearly rule out competitive partitioning of free phenyl radicals to benzene and iodobenzene in the low conversion photolyses. We conclude that there are two distinct paths for the formation of phenyl products.[24] Since the low conversion experiments show that iodobenzene does not have its origin in a reaction of phenyl radicals with triiodide in solution, we distinguish these paths as nondiffusive (C_6H_5I formed in a solvent cage) and diffusive (C_6H_6 formed in solution).

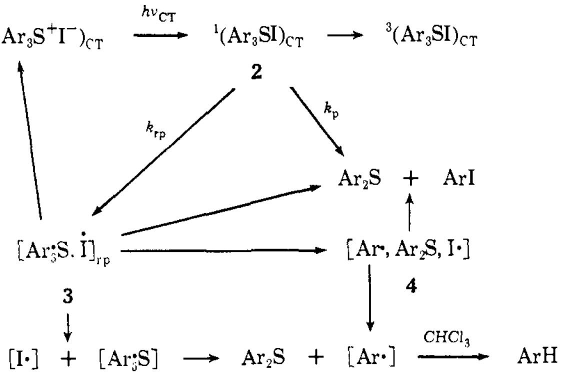
The simplest scheme accommodating all of the experimental observations involves partitioning of an intermediate (X) retaining, as a minimum, both the phenyl group and the iodine (Scheme I). The product ratio is simply the ratio of diffusive to nondiffusive paths and is, therefore, independent of per cent conversion. Unfortunately, the present data do not permit further refinement of the mechanism. In particular, the number of species preceding X, the nature of X, and the number of steps between X and the products remain unknown.

Scheme I



Consideration of a theoretical scheme, derived from Weller's[5,6] work, provides some insight into the possibilities and the complexities (Scheme II). The manifold of pathways outlined in Scheme II provides several intermediates which fit the requirements on X. For example, the CT singlet, **2**, might partition between nondiffusive collapse to diphenyl sulfide and iodobenzene, k_p, and electron transfer to give a radical pair, k_{rp}. Diffusive separation of this radical pair, **3**, would give $Ar_3\dot{S}$ in solution which could fragment to diphenyl sulfide and a phenyl radical. Similar competitions can be imagined with **3** and **4** as branch points for nondiffusive and diffusive pathways yielding iodobenzene and benzene, respectively. The importance of the triplet state in product formation is unknown. However, partitioning of the excited state between singlet and triplet, with the former yielding iodobenzene and the latter ultimately yielding benzene, would also be consistent with the data. Furthermore, the triplet might have a series of reaction pathways similar to those described for the singlet.

Scheme II



The photolysis of triarylsulfonium salts in methanol and ethanol has been described previously.[10a,b] Two important photochemical pathways were proposed. One path involved direct cleavage of the cation to a diarylsulfinium radical cation and an aryl radical; the other proposed an electron transfer step leading to a triarylsulfur radical and a halogen atom. These studies were carried out to high conversions at 254 nm. It is clear from the wealth of products, the poor mass balances, and the absorption spectra of starting materials and products, that secondary photolyses are important under these conditions. It is difficult, therefore, to make direct comparisons of the previous results with ours. These authors did, however, observe a significant effect of the nature of the anion (*e.g.*, I^- *vs.* Cl^-) on the extent of photodecomposition of the cation and on the nature of the products. Differences in the ultraviolet spectra of triphenylsulfonium chloride and bromide with respect to the iodide (all in methanol) were interpreted as showing that "the iodide and triphenylsulfonium ions interact strongly with each other, and this probably means that tight ion pairs predominate even in very dilute (methanolic) solution."[10a] Several effects, both in the photodecomposition and in the reactions of sulfonium iodides with bases, were interpreted in terms of this contact ion pair. The data cited in the present paper clearly contradict the importance of a contact triphenylsulfonium iodide ion pair in dilute methanol solution. In fact, the quoted special differences[10a] are simply due to absorption by iodide ion. This is readily concluded from the observation that the spectrum of a solution of potassium iodide and triphenylsulfonium perchlorate in methanol is superimposable with a spectrum obtained by placing the salts in separate cells in the same beam of the spectrophotometer (potassium perchlorate is transparent in the region under con-

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(23) $[I_3^-]$ ~ 5 × 10^{-3} *M* was estimated after 71% photolysis of 5 × 10^{-2} *M* **1** in chloroform by using the absorbance at 360 nm and the reported[20] extinction coefficient of I_3^- in chloroform.

(24) The thermal decomposition of PAT in chloroform in the presence of 5 × 10^{-2} *M* triphenylsulfonium iodide (**1**) gives benzene (64%) and only traces of iodobenzene (0.5%). This control rules out a reaction of phenyl radicals with iodide ion as the source of the iodobenzene in the photolysis of **1**. We thank R. B. Jordan for this experiment.

sideration). Thus, direct excitation of contact (charge transfer) ion pairs are not important in the photolysis of dilute solutions of triphenylsulfonium iodide in methanol. It is important to note, however, that the excited CT state might be indirectly populated by CT quenching of the excited triphenylsulfonium cation by iodide ion.[5,6] The manifold of intermediates outlined in Scheme II might, therefore, be pertinent to photolyses in both chloroform and methanol, even though the points of entry would be different.

In conclusion, the spectroscopic and photolytic studies described in this paper clearly demonstrate the involvement of an excited charge transfer complex in the photodecomposition of triphenylsulfonium iodide in chloroform. Further studies will be required to distinguish the detailed pathways by which the excited CT complex is transformed to products.

Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 421 infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian Model A-60 (60 MHz) spectrometer. Ultraviolet and visible spectra were recorded on a Cary Model MS 11 spectrophotometer. Gas-liquid chromatographic analyses were performed on F & M Models 700 and 720 dual column instruments equipped with thermal conductivity detectors and on a Perkin-Elmer Model 900 dual column instrument equipped with a flame ionization detector. All analyses were carried out on 0.25-in. diameter aluminum columns using helium as the carrier gas. Mass spectra were recorded on an Hitachi Perkin-Elmer Model RMU-6E mass spectrometer by Mrs. Eloise Rohner. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., or by Micro-Tech Laboratory, Skokie, Ill.

Chemicals. All reagents and solvents used were reagent grade and, unless noted otherwise, were used without further purification.

Triphenylsulfonium iodide was prepared by anion exchange between potassium iodide and triphenylsulfonium bromide.[25,26] The compound gives a 1.5° range decomposition point between 237 and 265° depending on the rate of heating and the initial temperature of the bath: lit.[26] mp 250°. The infrared spectrum of the compound is superimposable with the portion of the spectrum given in the literature (1250–667 cm^{-1})[26]: ir (KBr) 3070 (m), 3000 (m), 1595 (w), 1580 (w), 1475 (s), 1445 (s), 1315 (m), 1295 (w), 1175 (m), 1160 (m), 1095 (w), 1065 (m), 1020 (m), 995 (s), 935 (w), 840 (w), 770 (s), 760 (s), 735 (s), 680 (s) cm^{-1}.

Anal. Calcd for $C_{18}H_{15}IS$: C, 55.39; H, 3.87; I, 32.51; S, 8.22. Found: C, 55.36; H, 4.23; I, 32.49; S, 8.24.

Triphenylsulfonium perchlorate was prepared by anion exchange between triphenylsulfonium bromide and perchloric acid. Triphenylsulfonium bromide (0.559 g, 1.62×10^{-3} mol) was dissolved in 10 ml of water and the solution was filtered. A 10-ml aqueous solution of 70% perchloric acid was added dropwise to the filtrate. The precipitate, which formed immediately, was collected and washed with 2-ml portions of ice–water until the washings were neutral to Fisher Alkacid Test Paper. The crude compound was dissolved in excess warm acetone and the solution was concentrated by boiling. Water was added to the boiling acetone and the solution was then cooled to 5°. The resulting crystals were collected and dried for 24 hr at room temperature over calcium chloride at 0.1 mm to give triphenylsulfonium perchlorate: 0.475 g (81%); ir (KBr) 3080 (m), 3040 (w), 1585 (m), 1475 (s), 1445 (s), 1400 (w), 1315 (m), 1290 (w), 1180 (m), 1100 (s), 1020 (n), 995 (s), 940 (m), 925 (w), 845 (w), 835 (w), 750 (s), 700 (m), 680 (s), 635 (s), 625 (s), 620 (s), 610 (m) cm^{-1}.

Anal. Calcd for $C_{18}H_{15}ClO_4$: C, 59.58; H, 4.16. Found: C, 59.38; H, 4.16.

Approximately 10 mg of the perchlorate salt was pounded with a hammer on a metal block. Explosion occurred on the eighth blow. When the salt is heated on a metal spatula with a Bunsen burner, the salt melts and sparks, but a violet explosion does not occur. Because of the potential hazard of the perchlorate salt, all preparations and purifications were done on a small scale behind a shield. Small quantities of the salt were stored in plastic bottles in wooden boxes. The uv spectrum in chloroform shows maxima at 268 nm (ϵ 4750) and 276 (3270); $\epsilon_{300} < 20$. The uv spectrum in methanol shows maxima at 267 nm (ϵ 4090) and 275 (2900); $\epsilon_{300} < 20$.

Triphenyloxonium iodide was prepared by an anion exchange between triphenyloxonium fluoroborate[27] and potassium iodide. Triphenyloxonium fluoroborate, 0.787 g (2.35×10^{-3} mol), was dissolved in 300 ml of water at 60°. To the reaction flask was added a solution of 67.0 g (4.45×10^{-1} mol) of potassium iodide in 50 ml of water. The solution was stored at 0° for 12 hr. The resulting brown crystals were collected, and the solution was concentrated to approximately 100 ml by rotoevaporation at 60° and 25 mm. The concentrated solution was stored at 0° for 12 hr and a second crop of brown crystals was collected. The crystals were combined, washed with water, and dried over calcium chloride at 0.1 mm to yield 0.67 g (76%) of crude triphenyloxonium iodide. The brown crystals were dissolved in acetone and precipitated by the addition of ether to yield a white sandy solid. The solid was recrystallized from acetone–ether to yield 0.55 g (62% overall) of triphenyloxonium iodide: ir (KBr) 3050 (m), 1560 (m), 1475 (s), 1460 (m), 1130 (m), 1090 (s), 1020 (s), 990 (s), 910 (m), 860 (s), 750 (s), 740 (s), 730 (m), 680 (s) cm^{-1}.

Anal. Calcd for $C_{18}H_{15}IO$: C, 57.77; H, 4.04; I, 33.91. Found: C, 57.53; H, 4.14; I, 33.92.

Uv spectra: $(C_6H_5)_3O^+I^-$ in CH_3OH: maxima at 254 nm (ϵ 912), 257 (905), and 263 (584); $\epsilon_{275} < 15$. $(C_6H_5)_3O^+I^-$ in $CHCl_3$ (1.49×10^{-4} *M*): no maxima; ϵ_{275} 5440, ϵ_{295} 2950, ϵ_{330} 167. $(C_6H_5)_3O^+BF_4^-$ in CH_3OH: maxima at 252 nm (ϵ 646), 257 (677), 263 (423); $\epsilon_{272} < 20$. $(C_6H_5)_3O^+BF_4^-$ in $CHCl_3$: maxima at 255 nm (ϵ 933), 257 (971), 263 (533); $\epsilon_{272} < 30$.

Phenylazotriphenylmethane was used as supplied by Mr. James Hepinstall.[28]

Benzophenone (Eastman), White Label grade, was recrystallized three times from ethanol–water and once from hexane.

trans-**Stilbene** (Eastman), scintillation grade, was recrystallized twice from cyclohexane.

Apparatus and Experimental Techniques. Care was taken to protect all light-sensitive compounds from premature undirected decomposition. Solutions were prepared in a dark room with the aid of light provided by an Eastman Kodak brownie darkroom lamp, Model B. When a solution was prepared, the amount of compound weighed was such that the weighing error was less than 1%. Dilute solutions were prepared by quantitative dilution of concentrated solutions.

Solutions of triphenylsulfonium iodide and iodine in chloroform were prepared. Molar extinction coefficients (395 nm) were calculated on the assumption that all of the iodine was converted to triiodide ion; this is a limiting case that results in a minimum value for the extinction coefficient. When the molar extinction coefficient is taken as 1.09×10^4 (av) and the observable absorbance as 0.020, the limit of detection for triiodide ion is 2×10^{-6} *M*. If triiodide ion was detected at times when no decomposition of triphenylsulfonium iodide should have occurred, the experiment was discontinued or the presence of triiodide was considered in the interpretation of the results.

The ultraviolet spectrum of a 2.54×10^{-4} *M* solution of the triphenylsulfonium iodide in chloroform was determined. The solution was stored in a glass-stoppered volumetric flask in a dark cupboard for 7 days and then the spectrum was redetermined. The two spectra were essentially identical and no decomposition was observed. A related experiment showed the sulfonium iodide in chloroform to be stable to the darkroom lamp.

The optical path lengths of the cells used in the spectroscopic studies were stated by their manufacturers to be approximately 10, 5, 1, and 0.1 mm. The relationships of the cells were determined experimentally using standard solutions. A correction factor of −17.9% was applied to data obtained with the 0.1-mm cell.

All photolyses were carred out on degassed samples in Pyrex tubes. Degassing was accomplished by four freeze–evacuate–thaw cycles with the manifold pressure about 0.05 mm.

Photolysis was accomplished with a 450-W quartz Hanovia medium-high pressure mercury vapor lamp (Type L, Catalog No. 679A-36). The lamp was placed inside a Pyrex immersion well

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(25) B. S. Wildi, S. W. Taylor, and H. A. Potratz, *J. Amer. Chem. Soc.*, 73, 1965 (1951).

(26) W. A. Bonner, *ibid.*, 74, 5078 (1952).

(27) K. G. Harbison, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1966.

(28) J. Hepinstall, Ph.D. Thesis, University of Rochester, 1971.

Table V. Analysis for Triphenylsulfonium Ion in the Presence of Reaction Products

Soln no.	$10^4[1]$, *M*	$10^3[C_6H_6]$, *M*	$10^4[C_6H_5I]$, *M*	$10^3[C_6H_5SC_6H_5]$, *M*	$10^4[I_2]$, *M*	ϵ_{620}
1	9.27	1.52	8.38×10^{-4}	11.3	5.18×10^{-4}	806
2	9.27	0	0	0	0	831
3	7.42	1.21	6.71×10^{-4}	0.906	4.14×10^{-4}	827
4	7.42	0	0	0	0	832
5	5.56	1.21	6.71×10^{-4}	0.906	4.14×10^{-4}	831
6	5.56	0	0	0	0	830

containing a Corning uranium glass filter sleeve. The filter absorbs more than 99.5% of the light below 320 nm and less than 10% at 360 nm. The lamp was cooled by circulating distilled water through the jacket of the immersion well. A Rayonet Model MGR-500 merry-go-round was used to rotate the reaction tubes around the lamp. The tubes were cooled by two 100 ft^3/min fans and the temperature of the tubes never exceeded 30°.

Analytical Procedures. The concentration of triphenylsulfonium ion was determined from the optical density of the blue complex formed between triphenylsulfonium cation and cobalt thiocyanate.[18] An aqueous solution was prepared, 0.1 *M* in cobalt chloride and 0.5 *M* in ammonium thiocyanate. An aliquot of a photolyzed solution was diluted with chloroform to approximately 5×10^{-4} *M* in triphenylsulfonium cation. To 5 ml of the diluted reaction solution in a 25-ml volumetric flask was added 10 ml of the aqueous cobalt thiocyanate solution. The volumetric flask was stoppered with a ground-glass stopper and shaken on a Parr shaker. After 1 hr of shaking, an aliquot of the blue chloroform layer was removed and its optical density was measured at 620 nm. The concentration of triphenylsulfonium cation in the reaction solutions was calculated using Beer's law and a molar extinction coefficient obtained from standard solutions of triphenylsulfonium iodide. Six standard solutions of triphenylsulfonium iodide (three solutions at each of two different concentrations) were determined during the course of each analysis.

In order to obtain reproducible results, it was necessary to adhere rigorously to standard conditions. The aliquot of reaction solution was quantitatively diluted until the sulfonium cation concentration was approximately equal to the sulfonium cation concentration in the standard solutions (between 10^{-3} and 10^{-4} *M*). The volumes used in the analyses, 5 ml of diluted reaction solution and 10 ml of the cobalt thiocyanate solution, were quantitatively measured and the standard shaking time was 1 hr. Under these standard conditions, the calculated molar extinction coefficient (620 nm) for the blue complex is 811 ± 1.4 in the concentration range 1×10^{-3}-5×10^{-4} *M*.

Solutions of triphenylsulfonium iodide were analyzed for sulfonium cation in the presence of added reaction products, using the standard conditions described above. The results of the analyses are given in Table V. The presence of reaction products at their experimental concentrations does not interfere with the sulfonium cation analysis.

Unreacted triphenylsulfonium iodide was quantitatively removed from the photolysis solutions before glc analysis. A standard 50-ml buret that had been shortened to 10 ml was filled with ether and packed with 1.0 g of neutral Woelm aluminum oxide (activity grade 1). A reaction tube was cooled to approximately 5° and opened, and 2 ml of ether was added. A large portion of the unreacted triphenylsulfonium iodide precipitated. The alumina column was drained, the stopcock was closed, and the reaction solution was transferred to the column. The column was allowed to run dry and the eluent was collected in a 5-ml volumetric flask. The reaction tube and column were washed with an additional 1 ml of ether that was collected in the 5-ml volumetric flask to fill it to the mark. This volumetric solution was subsequently analyzed by glc.

Standard solutions of triphenylsulfonium iodide were subjected to the normal work-up procedures and glc analyses in order to demonstrate that the observed reaction products did not arise by glc pyrolysis of unreacted sulfonium salt.[19] Flame ionization analyses of the solutions after normal work-up showed less than 0.002% conversion and less than 0.45% conversion of sulfonium salt to diphenyl sulfide in two separate experiments.

Benzene, iodobenzene, and diphenyl sulfide were identified as products from the photolysis of triphenylsulfonium iodide by coinjection with authentic samples on at least three different glc columns. In addition, samples of each product were collected from the glc instrument and their mass spectra compared with those of commercial samples and samples collected by glc from a standard solution of authentic materials at concentrations approximating those of the reaction products. With the exception of peaks due to chloroform in the samples collected from chloroform solutions, each peak of relative intensity >3% in the spectrum of the reaction product was matched by a peak at the corresponding *m/e* in the spectra of the authentic samples. The converse was also true.

A method of equivolume injections was used for all quantitative glc analyses. Standard solutions were prepared such that the peak areas in standard and reaction solutions were comparable. At least three equivolume injections of each reaction and standard solution were made. An average concentration/area factor was obtained from three standard solutions of slightly different concentrations.

Normally, the reproducibility of peak areas for a given solution was in the 1-3% range (peak areas were measured with a Gelman planimeter). However, in analyses of reactions at less than 10% conversion, the baseline was not flat and the reproducibility of peak areas for a given solution was in the 3-5% range.

Reactions at conversions below 15% were analyzed using flame ionization detection, while reactions at conversions above 15% were analyzed using thermal conductivity detection. When thermal conductivity detection was employed, benzene was analyzed on a SF-96 column: 15 ft × 0.25 in., 20% on 60-80 Firebrick, 70°, He 65 ml/min, retention time 17 min. When flame ionization detection was employed, benzene was analyzed on a SF-96 column: 15 ft × 0.25 in., 20% on 60-80 Chromosorb A, He 65 ml/min using a temperature program of 70° for 12 min then heating at 6.5°/min to 115°, retention time 20.5 min.

Iodobenzene and diphenyl sulfide were analyzed by thermal conductivity detection using a Carbowax 20M column 2 ft × 0.25 in., 20% on 60-80 Firebrick, He 65 ml/min. The temperature of the column was 140° until iodobenzene eluted; the column temperature was then raised at the maximum heating rate of the oven to 240°; iodobenzene 7 min, diphenyl sulfide 15 min. Iodobenzene and diphenyl sulfide were analyzed by flame ionization using a SE-30 column 13 ft × 0.25 in., 20% on 60-80 Chromosorb W, acid washed, Silyl 8 treated, He 65 ml/min, temperature programmed from 100 to 230° at 8°/min, iodobenzene 4.5 min, diphenyl sulfide 20 min.

A stock solution was prepared: 2.035×10^{-1} *M* in benzene, 8.627 $\times 10^{-2}$ *M* in iodobenzene, and 7.730×10^{-2} *M* in phenyl sulfide in chloroform. Three aliquots of this stock solution were put through the alumina column work-up procedure described above for removal of unreacted sulfonium salt. The resulting solutions were compared with the stock solution by glc for loss of reaction products during the work-up procedure. The worst comparisons showed <3% loss of products on work-up; most samples were indistinguishable from the stock solution.

Competitive Reaction of Phenyl Radicals with Chloroform and Triiodide Ion or Iodide Ion. A. Two solutions containing triphenylsulfonium iodide (**1**), iodine, and phenylazotriphenylmethane (PAT) in chloroform were prepared, degassed, sealed in Pyrex tubes, and heated at 77° for 2.5 hr in the dark. The reaction solutions were worked up exactly as described for photolysis tubes and analyzed for benzene and iodobenzene by glc. The results are shown in Table VI.

B. Two solutions, 5.04×10^{-2} *M* in **1** in $CHCl_3$, were prepared. One solution contained 5.09×10^{-3} *M* PAT. Both solutions were

Table VI

10^2 initial concn, *M*			10^2 final concn, *M*	
PAT	[1]	I_2	C_6H_6	C_6H_5I
0.512	5.25	4.79	0.175	0.226
0.512	5.76	4.94	0.183	0.232

degassed, sealed in Pyrex tubes, and heated for 3 hr at 77° in the dark. The solutions were worked up and analyzed exactly as described for photolysis tubes. The blank tube contained a trace of benzene and 2.34×10^{-5} *M* iodobenzene. The reaction tube contained 3.27×10^{-3} *M* benzene (64%, based on PAT) and 4.68×10^{-5} *M* iodobenzene. The iodobenzene yield, corrected for iodobenzene in the blank, is 0.46%.

Quantum Yield for Triphenylsulfonium Iodide Decomposition. The quantum yield is based on the glc measurement of the yield of diphenyl sulfide. The actinometer employed the isomerization of *trans*-stilbene by benzophenone.[29]

Determination A. The reaction tubes, which contained chloroform solutions 1.04×10^{-1} *M* in triphenylsulfonium iodide, were prepared in the manner described previously. The reaction tubes were further wrapped with aluminum foil lined with yellow paper to protect them from the light of the oxygen torch while they were being sealed.

Actinometer tubes, which were benzene solutions of 9.97×10^{-2} *M* *trans*-stilbene and 9.98×10^{-2} *M* benzophenone, were prepared in the same manner as the reaction tubes.

The photolysis arrangement was as described above. The intensity of light available to the reaction tubes was decreased by partially wrapping the lamp well with aluminum foil lined with yellow paper. After the lamp had warmed up for 30 min, six actinometer tubes were placed on the merry-go-round. Three actinometer tubes were exposed for 45 min and two for 90 min. (One tube was wrapped in aluminum foil as a control.) During the exposure of the actinometer tubes, three tubes were photolyzed for 0 (a control tube), 1, and 4 min.

The actinometer tubes were analyzed by glc flame ionization detection on a Dow 11 column 6 ft × 0.25 in., 10% on Anachrom ABS 100–110, 175°, He 65 ml/min, *cis*-stilbene, benzophenone, and *trans*-stilbene 6.5, 10, and 12.5 min, respectively. The reaction tubes were analyzed by glc flame ionization detection in the manner described above. The per cent conversions of *trans*- to *cis*-stilbene for the 45 and 90 min exposures were 3.72 and 7.47%, respectively. The actinometer control tube wrapped in aluminum foil showed 0.042% conversion. Assuming a quantum yield of 0.56[29] for the conversion of *trans*- to *cis*-stilbene, the effective output of the lamp was 1.46×10^{-4} and 1.48×10^{-4} einstein $l.^{-1}$ min^{-1} based on the 45- and 90-min tubes, respectively. The results are given in Table IV. A second determination (B) at lower light intensity gave comparable results.

Table VII. Triphenylsulfonium Iodide in Methanol

10^4[**1**], *M*	ϵ_{275}, nm	10^4[**1**], *M*	ϵ_{275}, nm
6.58	298	131	285
13.2	289	197	282
26.3	292	263	283
39.5	290	328	287
52.6	292	411	288
65.7	286		

Spectroscopic Experiments. The ultraviolet spectrum of triphenylsulfonium iodide in ethanol free chloroform is superimposable with the spectrum of the salt in commercial chloroform containing approximately 0.75% ethanol. Therefore, commercial chloroform (Mallinkrodt AR) was used throughout.

The behaviors of triphenylsulfonium iodide and perchlorate were studied spectroscopically as a function of concentration and solvent. The results are summarized in Tables VII–XI.

Table VIII. Triphenylsulfonium Iodide in Methanol

10^2[**1**], *M*	ϵ_{305}, nm[a]	10^2[**1**], *M*	ϵ_{305}, nm[a]
5.02	76.4	17.3	134
5.08	74.3	24.1	174
6.72	90.8	33.7	242
9.88	108	48.6	277
		53.0	311

[a] Apparent ε calculated from initial salt concentration.

Table IX. Triphenylsulfonium Iodide plus Potassium Iodide in Methanol

10^2[**1**], *M*	Total $[I^-]10^2$, *M*	ϵ_{275}, nm[a]
3.91	3.91	287
3.91	16.8	314
3.91	31.9	329
3.91	Satd	362

[a] Apparent ε calculated from initial sulfonium salt concentration

Table X. Triphenylsulfonium Iodide in Chloroform

10^3[**1**], *M*	ϵ_{340}, nm[a]	10^3[**1**], *M*	ϵ_{340}, nm[a]
1.23	639	9.82	575
2.46	618	12.3	571
4.91	602	40.9	449
7.37	578	61.4	420

[a] Apparent ε calculated from initial salt concentration.

Table XI. Triphenylsulfonium Perchlorate in Chloroform

$10^3[(C_6H_5)_3S^+$-$ClO_4^-]$, *M*	ϵ_{275}, nm	$10^3[(C_6H_5)_3S^+$-$ClO_4^-]$, *M*	ϵ_{275}, nm
6.34	397	12.8	414
8.21	402	20.5	392
9.70	398	37.2	396
		41.1	402

Acknowledgment. This work was supported by a Public Health Service Grant, CA-06535, from the National Cancer Institute.

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(29) H. A. Hammond, D. E. Meyer, and J. L. R. Williams, *J. Amer. Chem. Soc.*, **91**, 5180 (1969).