

Photolysis of Triarylsulfonium Salts in Alcohol¹

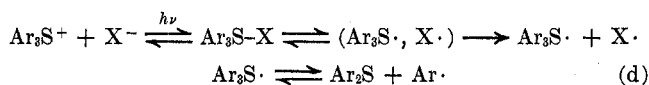
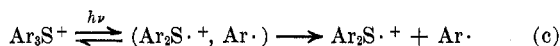
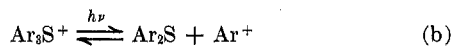
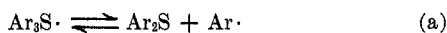
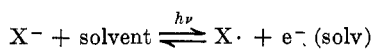
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Various triarylsulfonium salts have been subjected to photolysis in methanol and ethanol solutions, light of wavelength 2537 Å being used. The major products are aromatic hydrocarbons, aryl halides, aryl alkyl ethers, biaryls, diaryl sulfides, diaryl sulfoxides, and Brønsted acids. Diaryl disulfides and arylthiols are also produced, but it has not been possible to determine the yields of these compounds. The available evidence indicates that two major, primary photochemical reactions are taking place concurrently. One gives rise to a diarylsulfonium cation radical plus an aryl radical, and the other represents an electron-transfer reaction in which a triarylsulfur radical and a halogen atom are produced. The latter reaction is of greatest importance when triarylsulfonium iodides are photolyzed.

A complex mixture of products is produced when a triarylsulfonium salt is subjected to photochemical decomposition in alcohol solution. For example, photolysis of triphenylsulfonium chloride in ethanol solution for 61 hr, light of wavelength 2537 Å being used, gives benzene (10%), chlorobenzene (1%), phenetole (9%), biphenyl (1%), diphenyl sulfide (26%), diphenyl sulfoxide (2%), and hydrogen chloride (57%); unreacted triphenylsulfonium chloride is recovered in 34% yield. The photolysis of triphenylsulfonium chloride in methanol for 61 hr at 2537 Å affords benzene (10%), chlorobenzene (0.5%), anisole (11%), diphenyl (2%), diphenyl sulfide (30%), benzyl alcohol (0.2%), diphenylsulfoxide (2%), methylal (11%), and hydrogen chloride (49%); 33% of the starting sulfonium salt is recovered unchanged. Data for numerous additional photodecompositions of triarylsulfonium salts are given in Tables I and II. It is obvious that either aryl radicals or aryl cations are produced at some stage of these reactions, and four different pathways may be considered for the primary photochemical reactions.



Mechanism a, in which a solvated electron² is formed as a reactive species, might be expected to occur most readily when an easily photooxidized anion is present.³ Since essentially the same products (and ratios of products) are formed from both triphenylsulfonium chloride (expt 11, Table II) and triphenylsulfonium fluoroborate (expt 15, Table II), this mechanism appears to be an unlikely one. It can also be ruled out as a major pathway leading to products because the presence of nitrate ion (expt 4, 6, 14, 24) or of iodobenzene (expt 9) does not influence products or product ratios. These additives

are known to scavenge solvated electrons and would be expected to inhibit the reaction if mechanism a were operative.^{3b} Furthermore, HX is generated during each overall reaction, and the solvated electrons would be scavenged rapidly by protons.^{3b,4}

Pathway b, which represents a photochemical heterolytic dissociation of a C-S bond to give an aryl cation plus a diaryl sulfide, can be ruled out on the basis that the presence of iodine (expt 27, Table II), oxygen (expt 25, Table II), or diphenyl disulfide (expt 17, Table II) markedly inhibits the formation of benzene, halobenzene, anisole, and biphenyl. Since these additives are radical scavengers and would have no effect on the formation of an aryl cation by mechanism b,⁵ it can be concluded that such an ion is not being produced in the primary photochemical process.⁶

Mechanism d represents an electron-transfer reaction similar to those postulated to occur in related reaction systems.^{1,7} If such a mechanism were operative, the yields of aromatic hydrocarbon, aryl halide, and diaryl sulfide would correspond to the ease with which the counteranion can give up an electron to the associated acceptor cation. Thus, the amounts of these products should increase with change of anion in the order BF_4^- , NO_3^- , $\text{C}_2\text{H}_3\text{O}_2^-$, $\text{Cl}^- < \text{Br}^- < \text{I}^-$,^{3a,8} provided that solvent effects remain roughly the same. When ethanol is used as the solvent and a triphenylsulfonium salt as substrate, a good correlation between apparent photo-reducing power of the anion and the yields of benzene, diphenyl sulfide, and phenyl halide is observed (expt 1, 2, 3, and 4, Table I).⁹ When methanol, which is more

(4) L. M. Dorfman, "The Solvated Electron in Organic Liquids," ref 2, p 36.

(5) D. F. DeTar and M. N. Turetzky, *J. Amer. Chem. Soc.*, **77**, 1745 (1955).

(6) Evidence that the effect of these additives cannot be attributed to a quenching of excited sulfonium cations will be presented subsequently.

(7) (a) L. Horner and J. Dörge, *Tetrahedron Lett.*, 763 (1965); (b) C. E. Griffin and M. L. Kaufman, *ibid.*, 769, 773 (1965); (c) T. D. Walsh and R. C. Long, *J. Amer. Chem. Soc.*, **89**, 3943 (1967); (d) J. W. Knapczyk, G. H. Wiegand, and W. E. McEwen, *Tetrahedron Lett.*, 2971 (1965).

(8) (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966 p 268; (b) H. Friedman, *J. Chem. Phys.*, **21**, 319 (1953); (c) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience, New York, N. Y., 1963, p 328. The position of BF_4^- in this list represents an approximation.

(9) The presence of nitrate ion appears to catalyze the formation of benzene when ethanol is used as the solvent (expt 4 and 6, Table I) but not when methanol is the solvent (expt. 12, 14 and 24, Table II). That the increased yield of benzene observed in expt 6 (Table I) is not attributable to the presence of lithium ion or to an increase in the ionic strength of the medium is demonstrated by the results of expt 5, which show that the addition of lithium chloride has little effect on the yields of the products cited above. The influence of nitrate ion may not be due to its effect on a primary reaction but rather to its inhibitory effect on a secondary reaction that would otherwise consume the precursor of benzene.

(1) A preliminary report of a small portion of this work has been published: J. W. Knapczyk and W. E. McEwen, *J. Amer. Chem. Soc.*, **91**, 145 (1969).

(2) E. J. Hart, Symposium Chairman, "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965.

(3) (a) L. E. Orgel, *Quart. Rev.*, **8**, 422 (1954); (b) M. Anbar, "Reactions of the Hydrated Electron," ref 2, p 55.

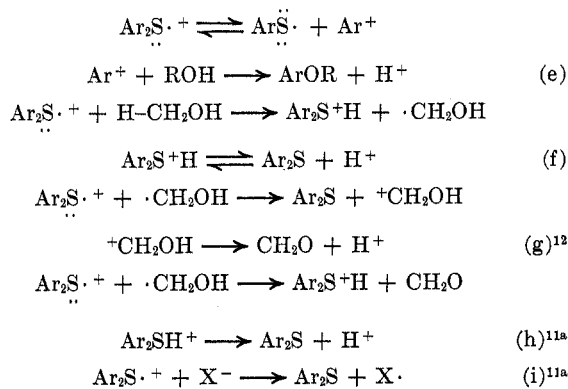
TABLE I^{a,b}
 IRRADIATION OF TRIPHENYLSULFONIUM SALTS FOR 61 HR IN ETHANOL

Expt	X	Additive	C ₆ H ₆	C ₆ H ₅ X	C ₆ H ₅ OC ₂ H ₅	C ₆ H ₅ -C ₆ H ₅	(C ₆ H ₅) ₂ S	Recovered		(C ₆ H ₅) ₂ S=O	Foot-note
								(C ₆ H ₅) ₂ S+X ⁻	H ⁺		
1	Cl		10	1.2	9	1.2	26	34	57	2	c
2	Br		23	7	4	1.4	36	24			d
3	I		31	36	2	1.4	52	~10			e
4	NO ₂		34		9	1.4	28	29			d
5	Cl	7.0 × 10 ⁻⁴									
		LiCl	10	1.2	9	1.2	27		49		f
6	Br	7.0 × 10 ⁻⁴									
		LiNO ₃	45	7	4	1.4	36		15	1	c, f
7	Br	1.4 × 10 ⁻³									
		CH ₃ CHO	32	7	5	1.9	33	41	51		f
8	Br	7.0 × 10 ⁻⁴									
		(C ₆ H ₅) ₂ S	21			0.5	44 ^g	51			f, d
9	I	7.0 × 10 ⁻⁴									
		C ₆ H ₅ I	32		2	0.8	53	10 ^h			f, d
10	(C ₆ H ₅) ₂ S		17			0.4	72	0	6		i

^a We elected not to express percentage yields in terms of amount of sulfonium salt reacted because of the uncertainty in determining the amount of unreacted sulfonium salt in some cases. ^b Many of the reactions summarized in this table were run in duplicate and some in triplicate to determine reproducibility, which was excellent. ^c Thiophenol could not be detected in these mixtures. ^d When no number appears under H⁺ it means that the mixture was not titrated. Brønsted acids were produced in every experiment. ^e Iodine was produced. The sulfonium salt was isolated in the form of the triiodide.^h ^f Values of additives in moles. ^g Based on 0.0014 mol. ^h Isolated as the triiodide, mp 137–138 [lit. mp 137.5–138: W. A. Bonner, *J. Amer. Chem. Soc.*, **74**, 5078 (1952)]. ⁱ Control experiment.

polar than ethanol,¹⁰ is used as solvent, the correlation also holds for the tri-*p*-tolylsulfonium salts, and, with the exception of the formation of benzene in expt 13 (Table II), for the triphenylsulfonium salts (expt 11, 12, 13, 28, and 29, Table II). However, the main drawback of mechanism d as the major primary photochemical process is that it offers no reasonable way to account for the large amounts of Brønsted acids formed in most of the reactions.

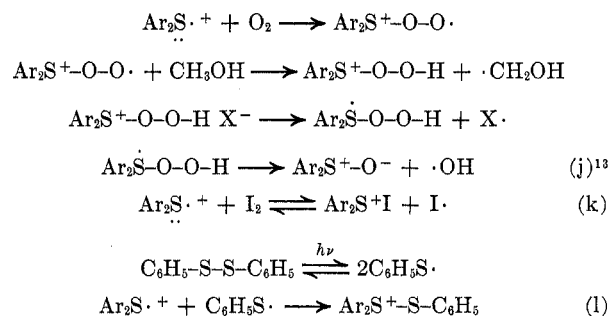
Mechanism c consists of a photochemical homolytic cleavage of the triarylsulfonium salt to give an aryl radical and a diarylsulfonium salt.¹¹ The diarylsulfonium cation might be expected to undergo further reactions, depending on the availability of the various reagents, by the following mechanisms, four of which (e through h) give rise to Brønsted acids.



(10) The dielectric constant for methanol at 20° is 33.6 as against 25.1 for ethanol.⁴

(11) (a) U. Schmidt, "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience, New York, N. Y., 1967, p 75; (b) H. J. Shine, ref 11a, p 93; (c) S. G. Cohen, ref 11a, p 33.

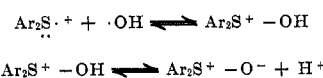
(12) A similar reaction has been reported to occur with a phenyl radical as the hydrogen abstracting agent.⁵ However, if phenyl radicals produced by mechanism d were responsible for the generation of the Brønsted acids, there would be a correspondence between the molar amounts of acid and benzene obtained. Clearly, there is no such relationship, as the molar amount of acid greatly exceeds that of benzene in each of the reactions of the triphenylsulfonium salts.



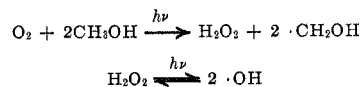
The inhibition of formation of alkyl aryl ether when radical scavengers (*e.g.*, oxygen, iodide ion, and the phenylthiyl radical^{11a}) are present can be explained in terms of reactions i, j, k, and l; *i.e.*, the scavengers intercept the diarylsulfonium cation radical before it has a chance to react by pathways e, f, g, and h.

A substantial amount of diphenyl sulfoxide was produced in the experiment where the reaction mixture was exposed to oxygen (expt 25, Table II). Although some of the sulfoxide may have arisen by photooxidation of diphenyl sulfide produced in the reaction mixture, most of it must have been formed from another precursor. The evidence for this statement consists of the observation that the yield of diphenyl sulfoxide in expt 25 (Table II) was 13%, but the yield of diphenyl sulfide

(13) An alternative mechanism for the formation of the diaryl sulfoxide is the following.^{11a}



It is also possible that hydroxyl radicals arise by the following pathway in the irradiated reaction mixture.



The bond dissociation energies of H-CH₂OH and H-C(CH₃)HOH are 24 and 21 kcal/mol, respectively, at 298°K.^{8a} Thus, energy considerations for these hydrogen abstraction reactions on methanol and ethanol would appear to be highly favorable.

TABLE II^a
 IRRADIATION OF (*p*-RC₆H₄)₃S⁺X⁻ FOR 61 HR IN METHANOL

Expt	R	X	Additive	C ₆ H ₅ R	<i>p</i> -X- C ₆ H ₄ R	<i>p</i> -R- C ₆ H ₄ OCH ₃	<i>p</i> -R- C ₆ H ₄	<i>p</i> -R- (C ₆ H ₄) ₂ S	Re- covered (<i>p</i> -R- C ₆ H ₄) ₂ - S ⁺ X ⁻	H ⁺	<i>p</i> -R- C ₆ H ₄ - CH ₂ OH	<i>p</i> -R- C ₆ H ₄ - S=O	CH ₂ - (OCH ₃) ₂	Footnote
11	H	Cl		10	0.5	11	2.0	30	33	49	0.2	2	11	
12	H	Br		13	2	7	1.0	37	30	43			17	
13	H	I		10	47	6	0.8	43		4	t	0.3	16	b, c, d
14	H	NO ₃		11		10	1.1	38	39					e
15	H	BF ₄		11		9	1.1	34	38			3	15	f, g
16	H	$\begin{array}{c} \text{O} \\ \\ \text{OCC}_6\text{H}_5 \cdot \\ 2\text{H}_2\text{O} \end{array}$		9		12	1.6	35					14	e
17	H	Cl	3.5 × 10 ⁻⁴ (C ₆ H ₅ S) ₂	3	0.1	2		22	75	52			6	h, i
18	H	Br	Pyrex vessel	8	0.5	t	0.1	12	78	9	t			b, j
19	H	Br	1.4 × 10 ⁻³ H ₂ O	15	2	9	1.7	33	31	44	t		19	b, i
20	H	Br	1.4 × 10 ⁻³ CH ₂ (OCH ₃) ₂	12	3	7	2	29	39	42	t			b, i
21	H	Br	7.0 × 10 ⁻⁴ (C ₆ H ₅) ₂ S	13	2	3	0.8	60	53	30			24	g, i
22	H	Br	7.0 × 10 ⁻⁴ NaOCOCH ₃	14	2	8	2.2	36			0.4	0.3	2	e, i
23	H	Br	7.0 × 10 ⁻⁴ NaOCOC ₆ H ₅	17	2	7	2.2	37			0.4		2	e, i
24	H	Br	7.0 × 10 ⁻⁴ LiNO ₃	13	2	2	1.1	38	33					e, i
25	H	Br	O ₂	6	5	0.6	0.5	32	26	51	t	13	41	b, k
26	H	I	7.0 × 10 ⁻⁴ NaI	9	70	3	0.4	48		2	t	0	19	b, c, i
27	H	NO ₃	7.0 × 10 ⁻⁴ I ₂	2	43	t	0.2	34		52		2	102	d, i
28	CH ₃	Br		30	3	8	4	43	13	55			21	
29	CH ₃	I		33	58	5	2	47	0	16			21	c
30	(C ₆ H ₅) ₂ S			13		0	1	78						l, e
31	(C ₆ H ₅) ₂ S		O ₂					4				6		m, n, k, e, j
32	H	Br		11	3	6	1.4	27	44	36	t		14	o

^a All reactions except expt 17 produced a solid yellow substance that precipitated on the sides of the reaction vessel. In all reactions several unidentified low-boiling and high-boiling products were also produced. ^b t = trace amount. ^c Iodine was also produced and isolated as triphenylsulfonium triiodide. ^d Methyl iodide was not found. ^e When no number appears under H⁺ it means that the mixture was not titrated. ^f An insoluble polymer film formed. ^g Thiophenol not detected. ^h 26% (based on 0.0007 mol) thiophenol found. ⁱ Values of additive in moles. ^j Control experiment. ^k The solutions were saturated with oxygen and sealed in an atmosphere of pure oxygen. ^l An insoluble oil was also produced. ^m Percentages based on 0.00035 mol of starting sulfide. ⁿ Artificial mixture also containing 5 × 10⁻⁵ mol of benzene, 2 × 10⁻⁵ mol of chlorobenzene, 1 × 10⁻⁵ mol of biphenyl, 2 × 10⁻⁴ mol of methylal, 2 × 10⁻⁴ mol of hydrochloric acid. ^o Reaction period 13.5 hr.

decreased only 5% as against the results of expt 12 (Table II). Also, in a control experiment in which diphenyl sulfide was irradiated in the presence of oxygen and an artificial mixture of reaction products, the yield of diphenyl sulfoxide was only 6% (expt 31, Table II). Thus, we suggest that much of the diphenyl sulfoxide produced in expt 25 arose by mechanism j or else by the alternative pathway depicted in footnote 13.¹⁴

As an alternative to pathway e for the formation of alkyl aryl ethers, consideration must be given to the possibility that an aryl radical adds to the oxygen atom of formaldehyde or acetaldehyde, generated as shown in eq g and h, to give a new radical, ArOĊHR, which then forms the ether by a suitable hydrogen abstraction reaction.¹⁵ This possibility is ruled out on the basis of the fact that the addition of relatively large amounts of acetaldehyde (expt 7, Table I) or methylal (expt 20,

Table II) to the reaction mixtures did not bring about any increase in the yields of ethers.

All of the reaction mixtures became acidic as the reaction progressed. However, there were significant differences in the amounts of titratable acids produced, depending on the nature of the anion present.¹⁶ Specifically, the amount of acid produced was least when iodide ion was present, intermediate in amount when bromide ion was present, and greatest with chloride. Since the Brønsted acids presumably arise *via* mechanism c followed by e through h, the anion effect implies strongly that pathway d competes with c as the primary process. As mentioned previously, pathway d would increase in importance with change of anion in the order Cl⁻ < Br⁻ < I⁻ and would not set in motion subsequent reactions which would produce any significant amounts of Brønsted acids.¹² In other words, the amount of Brønsted acid produced is a good measure of the extent

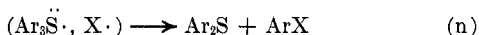
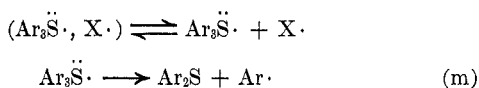
(14) These results also provide evidence that quenching of photoexcited triarylsulfonium cation is not a likely explanation for the inhibition of certain of the reactions when the additives are present.

(15) (a) M. S. Kharasch, D. Schwartz, M. Zimmermann, and W. Nudenberg, *J. Org. Chem.*, **18**, 1051 (1953); (b) F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **70**, 3258 (1948); (c) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 238 (1953).

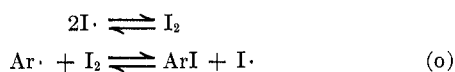
(16) The presence of buffers did not produce any significant effect on the ratios of products (expt 12, 16, 22, and 23, Table II). It should also be noted that a small amount of Brønsted acid is produced by the photodecomposition of the diaryl sulfide which is produced in the major sequences of reactions (expt 10, Table I).

of reaction proceeding by pathway c as the primary step. Indeed, in many of the experiments there is a good correspondence between the molar amounts of acid and the combined molar amounts of, for example, anisole and methylal formed. Specifically, 1 mol of acid should be produced/mol of anisole (eq e) and 2 mol of acid/mol of methylal (eq f, g, and h) produced. Thus, in expt 12 (Table II) a 41% yield of acid would be anticipated on the basis of this reasoning as against 43% actually found.

A comparison of the results of the reactions of tri-*p*-tolylsulfonium bromide and iodide in methanol solution (expt 28 and 29, Table II) with those of triphenylsulfonium bromide and iodide (expt 12 and 13, Table II) reveal that the former give a larger ratio of aromatic hydrocarbon plus biaryl to aryl halide than the latter. This is probably a reflection of the greater stability of the tri-*p*-tolylsulfur radical as against the triphenylsulfur radical.¹⁷ It is a reasonable assumption that the radicals produced by mechanism d are initially paired; *i.e.*, they exist in a solvent cage. The more stable the radicals that make up the radical pair, the greater is the likelihood of the radicals becoming free from one another and reacting with the solvent or other molecules external to the solvent cage, these reactions producing aromatic hydrocarbons and biaryls, among other products. This sequence of reactions starts with pathway m. On the other hand, when the radical pair consists of more reactive radicals, they tend to react within the solvent cage to produce an aryl halide plus a diaryl sulfide, as shown in the reaction pathway n.



In the reaction of the triarylsulfonium iodides, some iodine is produced by photochemically initiated redox reactions. When iodine is formed in this manner, at least some of the aryl iodide produced arises by the reaction pathway o.^{5,18} In fact, since aryl iodides are formed apparently at the expense of aromatic hydrocarbons and biaryls in the reactions of the triarylsulfonium iodides, pathway o might represent a substantial source of the aryl iodides produced.



Varying amounts of resinous materials were formed in each of the photochemical experiments. Thus, it is difficult to analyze the data with respect to material balance considerations, especially with regard to the organosulfur compounds. As a result of the photolysis of tri-*p*-tolylsulfonium iodide in methanol solution (expt 29, Table II), for example, the combined yield of toluene, *p*-iodotoluene, *p*-methoxytoluene, and di-*p*-tolyl was 98%, but the yield of di-*p*-tolyl sulfide was only 47%. Furthermore, no di-*p*-tolyl sulfoxide was found, nor was any tri-*p*-tolylsulfonium iodide recovered.

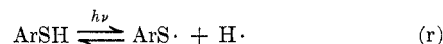
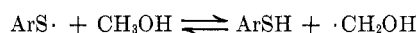
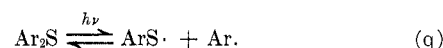
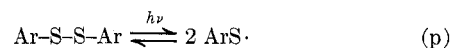
(17) A similar argument was used to explain differences in reactivities of tri-*p*-tolylsulfonium and triphenylsulfonium salts in reactions with sodium alkoxides.^{1,17}

(18) Under the conditions employed in these experiments, a significant amount of iodide ions would be converted to iodine atoms. Since hydrogen abstraction reactions of the iodine atoms would be reversible, the concentration of iodine atoms would probably be appreciable at all times.

A partial explanation for these results is the fact that the diaryl sulfide itself undergoes a photochemical reaction. By way of illustration, irradiation of diphenyl sulfide under the same conditions as employed for the tri-*p*-tolylsulfonium iodide reaction afforded benzene in 13% yield and biphenyl in 1% yield; diphenyl sulfide was recovered in 78% yield (expt 30, Table II).¹⁹

Trace amounts of thiophenols and diaryl disulfides were found in many of the reaction mixtures.²⁰ Diphenyl sulfoxide was found in yields ranging from 0.3 to 3.0% even in those systems where precautions were taken to exclude oxygen of the air (expt 1 and 6, Table I and 11, 13, 15, 22, and 27, Table II).

Inasmuch as diaryl disulfides and thiophenols absorb strongly in the 2537-Å region of the ultraviolet spectrum, and since arylthiyl radicals are produced from such compounds under these conditions as shown, for example, in eq p,²¹ it is probable that such radicals, which are also formed by irradiation of diaryl sulfides as shown in eq q,²² persist for an appreciable period of time. This would be so even in a solvent which is susceptible to hydrogen abstraction by such radicals owing to the continual renewal of the arylthiyl radicals, as shown in eq r.²³ This permits aromatic radical sub-



stitution reactions of the types shown in eq s and t to occur during extended irradiation periods and probably accounts for the formation of organosulfur compounds of high molecular weight, which are not detected by vapor phase chromatography.^{24,25}

(19) One of the referees suggested that product ratios (abundances) or individual yields, adjusted for recovered triarylsulfonium salt, the limiting reactant, should be used to compare the results of these experiments rather than conventional yields, which were actually used. Since we are not sure of the origin of some of our products, it is our opinion that the use of unrecovered triarylsulfonium salt as the "limiting reactant" may be misleading. Furthermore, on the basis of yields and product ratios, calculated according to the suggestions of the referee, we see no reason to change our conclusions about mechanisms of reaction.

(20) Through control experiments, we found that small amounts of diphenyl disulfide could not be detected by vapor phase chromatography inasmuch as the compound underwent decomposition at the injection port of the gas chromatograph. A partial analysis based on its decomposition products was possible only when the compound was present in large amount. Attempts to determine quantities of thiophenols and diaryl disulfides in the reaction mixtures by application of thin layer chromatography were unsuccessful owing to the complexity of the mixture.

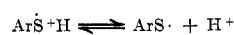
(21) (a) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill, New York, N. Y., 1962, p 42; (b) J. G. Calvert and J. N. Pitts, ref 8a, p 488.

(22) (a) L. Horner and J. Dörge, *Tetrahedron Lett.*, 757 (1963); (b) N. Kharasch and A. I. A. Khodair, *Chem. Commun.*, 98 (1967).

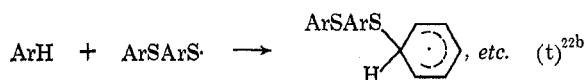
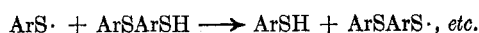
(23) (a) J. G. Calvert and J. N. Pitts, ref 8a, p 490; (b) W. E. Haines, G. L. Cook, and J. S. Ball, *J. Amer. Chem. Soc.*, **78**, 5213 (1956).

(24) Solutions of dimesityl disulfide in 2-propanol in the presence of benzophenone are readily converted to an equilibrium mixture of about 70% mesitylthiol and 30% dimesityl disulfide when irradiated: S. G. Cohen, ref 11a, p 42. Apparently the presence of methyl groups in the *ortho* and *para* positions inhibit aromatic radical substitution reactions of the types depicted in eq s and t.

(25) Since thiophenols are known to give rise to solvated electrons in suitable solvents, the following pathway for the generation of arylthiyl radicals is also a possibility.

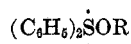


Cf. L. I. Grossweiner and H. I. Joschek, ref 2, p, 279.



All of the photochemical reactions listed in Tables I and II except the last one (expt 32, Table II) were allowed to continue for a period of 61 hr. In expt 32, the reaction mixture was irradiated for only 13.5 hr. Comparison of the results of this experiment with those of expt 12 (Table II) reveals relatively little difference in the yields of the various products. Nevertheless, a significant quantity of unreacted triphenylsulfonium bromide was recovered even after the 61-hr period of irradiation. A possible explanation is that, owing to the formation of products which strongly absorb light of the wavelength used in the irradiation relatively early in the period of irradiation, much of the photochemical energy needed for the primary process is unavailable at a later time. For example, the presence of diaryl disulfides or arylthiols and the occurrence of reactions of the types depicted in eq p and r could cause inhibition of the primary processes c and d. Indeed, when diphenyl disulfide was added to a typical reaction mixture (expt 17, Table II), the amount of triphenylsulfonium salt recovered after a 61-hr period of irradiation increased markedly (*cf.* expt 11, Table II).²⁷

The addition of diphenyl sulfide to the solutions of triphenylsulfonium bromide prior to irradiation also leads to a marked increase in the recovery of starting material (*cf.* expt 2 and 8, Table I, and 12 and 21, Table II). A reversal of eq d could account for this result. A similar explanation has been suggested for analogous results observed in the photodecomposition of phosphonium salts.^{7b} Also, some evidence has been presented in the literature for the addition of an alkoxy radical to diphenyl sulfide to give



as an unstable intermediate in certain reactions.²⁸

(26) Y. Schaafsma, A. F. Bickel, and E. C. Kooyman, *Tetrahedron*, **10**, 76 (1960).

(27) Actually, it is not known whether diphenyl disulfide or the products of its photochemical dissociation are acting as filters, or whether the disulfide is quenching an excited state of one of the primary photochemical decomposition reactions.

(28) R. J. Gritter and D. J. Carey, *J. Org. Chem.*, **29**, 1160 (1964).

Experimental Section

All of the sulfonium salts were prepared as described in a previous paper,¹ with the exception of triphenylsulfonium benzoate.

Triphenylsulfonium Benzoate Dihydrate.—To 3.65 g (0.0095 mol) of triphenylsulfonium iodide dissolved in 40 ml of methanol was added 2.2 g (0.01 mol) of silver oxide. The mixture was allowed to stir rapidly for 4 hr in the dark. The precipitate of silver iodide and unreacted silver oxide was removed by filtration, and to the clear filtrate was added a solution of 1.2 g (0.01 mol) of benzoic acid in 5 ml of methanol. The solution was evaporated to dryness. The resulting oil was induced to crystallize from methylene chloride-ether mixtures. The yield of the purified substance, mp 288–289°, was 0.91 g (20%).

Anal. Calcd for $\text{C}_{25}\text{H}_{24}\text{SO}_4$: C, 68.46; H, 5.99; S, 7.31. Found: C, 68.48; H, 5.90; S, 7.29.

Irradiation of Triarylsulfonium Salts.—The sulfonium salts, 7.00×10^{-4} mol, and the appropriate additives were dissolved in 3.00 ml of the appropriate anhydrous solvent²⁹ which had previously been deaerated by bubbling a fine stream of dry, oxygen-free nitrogen through the refluxing solution for 4 hr. The solutions were sealed under nitrogen in 12-mm quartz tubes and irradiated by a bank of sixteen Rayonet photochemical reactor lamps no. RPR of which 90% of the intensity of the light is of wavelength 2537 Å. Each solution was homogeneous at the start of reaction. At the end of the reaction period the tubes were opened and the contents were analyzed directly by gas chromatography, an F & M Model 609 flame ionization gas chromatograph being used. To obtain proper separations of the volatile materials, three different columns had to be used: (1) a 6-ft 5% Apiezon L column for most of the components, (2) a 6-ft 20% Carbowax 20M column for determination of methylal, and (3) a 6-ft 15% Ucon 50 column for determination of bromobenzene in the presence of phenetole. The concentration of Brønsted acids was determined by pipetting a 1.00-ml aliquot of the sample into 50 ml of water and titrating to the phenolphthalein end point with 0.1500 N sodium hydroxide solution. The amount of unreacted sulfonium salt was found by adding a 1.00-ml aliquot of the reaction mixture to 45 ml of anhydrous ether. After several hours the solution was decanted from the crystals that had formed, and the crystals were washed with 40 ml of anhydrous ether, dried, and weighed. In most cases a melting point and an infrared spectrum were taken of the solid to confirm its identity.

Registry No.—Triphenylsulfonium benzoate, 25183-63-5. Table I—expt 1 (salt), 4270-70-6; 2 (salt), 3353-89-7; 3 (salt), 3744-08-9; 4 (salt), 19600-48-7; 10 (salt), 139-66-2. Table II—expt 15 (salt), 437-13-8; 28 (salt), 3744-11-4; 29 (salt), 22417-23-8.

Acknowledgment.—This work was supported by a grant from the National Science Foundation. Miss Rebecca Dike carried out many of the vpc analyses and titrations.

(29) The alcohols were dried by the method of Lund and Bjerrum as described in A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1956, p 167.