

Comparison of the Photochemistry of Diarylchloronium, Diarylbromonium, and Diaryliodonium Salts

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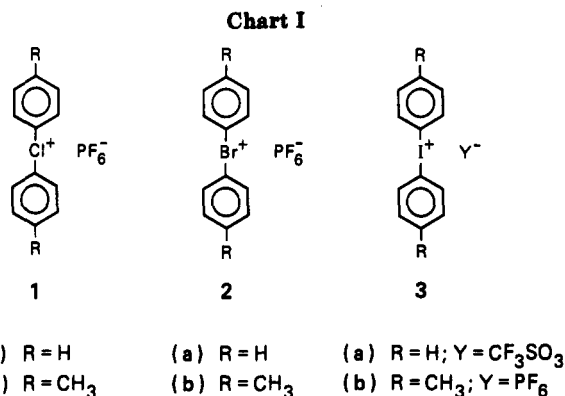
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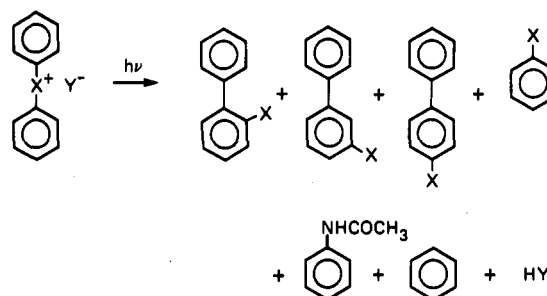
The direct and triplet-sensitized photochemistry of diphenylchloronium, diphenylbromonium, bis(4-methylphenyl)chloronium, and bis(4-methylphenyl)bromonium salts was studied. Direct photolysis of the diarylhalonium salts gave haloarene 2-, 3-, and 4-halobiaryls, and acetanilide, predominantly from a heterolytic cleavage mechanism via the aryl cation-haloarene pair, via in-cage recombination and cage-escape reactions. However, triplet-sensitized photolysis gave haloarene, 2-, 3-, and 4-halobiaryl, and reduced arene mainly from homolytic cleavage to the arene radical-haloarene radical cation pair, which also gave in-cage recombination and cage-escape products. There is evidence for singlet-triplet interconversion of the excited states by spin-orbit coupling and interconversion of the singlet-triplet radical pairs by spin-spin coupling. In addition, electron transfer between the singlet arene cation-haloarene and arene radical-haloarene radical cation pairs is also possible. The effect of halogen and arene substituent on these interconversions is discussed.

Introduction

Onium salts, especially triarylsulfonium and diaryliodonium salts, have found wide technological use in industry as photoinitiators for cationic polymerization^{1,2} and as "photoacid" generators to catalyze deprotection and depolymerization reactions for imaging systems.³ We recently discovered that triarylsulfonium salts, upon direct irradiation, produce mainly in-cage recombination products similar to those of the photo-Fries reaction,⁴ in addition to the cage-escape products.⁵⁻⁷ In contrast to the photo-Fries reaction, which occurs by homolytic cleavage, the direct photolysis of triarylsulfonium salts occurred mostly by heterolysis of the singlet excited sulfonium salt, with homolysis occurring to a minor extent.⁷ Triplet sensitization of the sulfonium salts gave no recombination products and gave exclusively escape products arising from homolysis of the sulfonium salt,⁸ whereas sensitization with naphthalene occurs by electron transfer from the singlet excited state of the sensitizer and gives recombination products by an in-cage back-electron-transfer mechanism.⁹ The formation of recombination products from onium salt photolysis is not unique to triarylsulfonium salts. Alkylarylsulfonium salts, alkylarylarsonium salts, and diaryliodonium salts have been reported to give recombination products.¹⁰⁻²¹ However, diaryliodonium salts produce



Scheme I. Products from Irradiation of Diphenylhalonium Salts

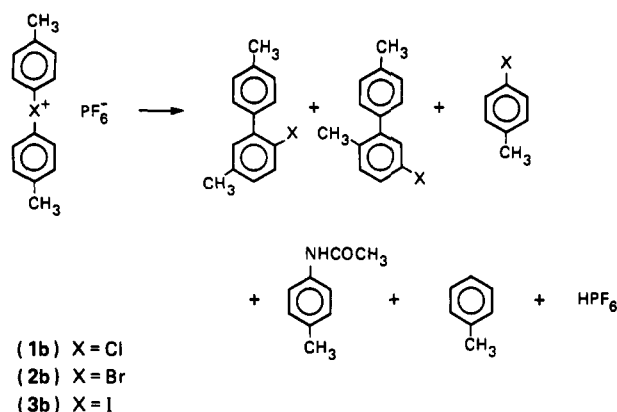


- (1a) X = Cl; Y = PF₆
 (2a) X = Br; Y = PF₆
 (3a) X = I; Y = CF₃SO₃⁻

recombination products upon both direct and sensitized irradiation^{18,21} and produce products from both heterolytic and homolytic cleavage of the iodonium salt under both conditions.^{20,21} To account for the different photochemistry of the sulfonium and iodonium systems, it is proposed that the initially formed intermediates in the iodonium photolysis, the phenyl cation-iodobenzene pair, could interconvert with the singlet phenyl radical-iodobenzene

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Scheme II. Products from Irradiation of Bis(4-methylphenyl)halonium Salts

radical cation pair²¹ and that the singlet and triplet phenyl radical-iodobenzene radical cation pairs could also interconvert.^{18,21} The triarylsulfonium salt system does not undergo this interconversion. A study of the photochemistry of other diarylhalonium salts should provide further insight into the factors that affect the ability of onium salts to produce recombination products and to relate these factors to the overall efficiency of the photoreaction. To date only two studies on the photochemistry of diarylchloronium or diarylbromonium salts have been reported. Crivello evaluated these salts as photoinitiators in epoxy resins and detected bromobenzene, benzene, biphenyl, and acid from direct photolysis of diphenylbromonium hexafluorophosphate.²² In a preliminary study, we have detected recombination products from direct irradiation of these salts.²³ We report here the direct and triplet-sensitized photolysis of diarylchloronium and diarylbromonium salts.

Results

Two series of salts were prepared, the diphenyl- and the bis(4-methylphenyl)halonium salts. The bromonium and chloronium salts were prepared by the decomposition of the appropriate diazonium salt with the haloarene and trifluoroacetic acid, followed by precipitation of the desired hexafluorophosphate salt from water²⁴ (Chart I). The direct photolysis of the diphenylhalonium salts was first qualitatively investigated. Photolysis of all of the salts resulted in formation of arene (either benzene or toluene), haloarene, and recombination products (Scheme I). In the case of diphenylchloronium hexafluorophosphate, the recombination products produced were 2-, 3-, and 4-chlorobiphenyl, which correspond formally to migration of a phenyl from chlorine to the other aromatic ring, followed by loss of HPF₆. The chlorobiphenyls and bromobiphenyls were identified by comparison with authentic commercial materials. Acetanilide, a product that indicates the intermediacy of phenyl cation, was also produced. Biphenyl was not a significant photoproduct.

In the case of the (4-methylphenyl)halonium series, analogous recombination products, 5-halo-2,4'-dimethylbiphenyl and 2-halo-4',5-dimethylbiphenyl, were obtained upon direct irradiation (Scheme II). The formation of these compounds was confirmed by comparison with iso-

Table I. Product Quantum Yields upon Direct Irradiation of 0.01 M Salt Solutions in Acetonitrile, $\lambda = 248 \text{ nm}^a$

compd (Ar ₂ X ⁺ salt)	total	ArX	2-XBP	3-XBP	4-XBP
Ph ₂ Cl ⁺ PF ₆ ⁻	0.79	0.663	0.0595	0.0392	0.0258
Ph ₂ Br ⁺ PF ₆ ⁻	0.82	0.670	0.0762	0.0454	0.0290
Ph ₂ I ⁺ Tf ⁻	0.54	0.400	0.104	0.018	0.021
4-Tol ₂ Cl ⁺ PF ₆ ⁻	0.73	0.623	0.036	0.070	-
4-Tol ₂ Br ⁺ PF ₆ ⁻	0.74	0.606	0.082	0.047	-
4-Tol ₂ I ⁺ PF ₆ ⁻	0.45	0.320	0.104	0.028	-

^a Ph = phenyl; 4-Tol = 4-methylphenyl, XBP = halobiphenyl.

Table II. Stability of Phenyl Cation-ArX Pair vs Phenyl Radical-ArX Radical Cation Pair

compd	ArX E _{1/2} ^a (vs SCE)	ΔG , kcal mol ⁻¹ ^b	ArH:ArX ^c singlet	ArH:ArX ^d triplet	spin density ^e
Ph ₂ Cl ⁺	2.37	-6.7	0.034	0.93	0.23
Ph ₂ Br ⁺	2.28	-4.6	0.09	0.93	0.30
Ph ₂ I ⁺	2.07	0.2	0.20	0.50	ca. 0.46
4-Tol ₂ Cl ⁺	2.07	0.2	0.064	0.50	-
4-Tol ₂ Br ⁺	2.02	1.4	0.11	0.83	0.27
4-Tol ₂ I ⁺	1.83 ^f	5.8	0.38	0.87	ca. 0.41

^a For oxidation of ArX in CH₃CN, from ref 34. ^b For electron transfer between the aryl cation-haloarene pair and the aryl radical-haloarene radical cation pair. $\Delta G < 0$, aryl cation pair more stable; $\Delta G > 0$, aryl radical pair more stable (see text). ^c By direct irradiation (CH₃CN). ^d By triplet energy transfer (acetone). ^e Spin density on halogen, from ref 33. ^f Calculated from vertical IP, from ref 35.

lated samples of these compounds prepared by a Gomberg-Bachmann reaction. The identity of the two isomers was apparent by ¹H NMR. For all of the 5-halo-2,4'-dimethylbiphenyls compared with the 2-halo-4',5-dimethylbiphenyls, the 2-methyl group appears at higher field than the 5-methyl group due to the deshielding by the adjacent aromatic ring. The 4'-methyl group appears at lowest field (see Experimental Section).

Quantum yields were then determined for these compounds upon direct irradiation ($\lambda = 248 \text{ nm}$) in acetonitrile. The results are shown in Table I, along with previously reported data for diaryliodonium salts.²¹ For the diphenylhalonium series, the total halogen-containing-product quantum yield, which is assumed to be the quantum yield of disappearance, is about the same for the chloronium and bromonium compounds, 0.79 and 0.82, respectively. Diphenyliodonium is less efficient, at 0.54. The fraction of the halobenzene escape product relative to total halogen-containing products decreases from 84% for the chloronium to 82% for the bromonium and down to 74% for the iodonium. The distribution of the recombination products also varies down the series (Table IV). The ratios of 2- to 3- to 4-halobiphenyl for the chloronium salt are 48:31:21; for the bromonium, there is a similar ratio of 51:30:19; and for the iodonium, there is a different distribution of 73:13:14. Thus, the diphenyliodonium photolysis produces relatively more 2-halobiphenyl and less 3-halobiphenyl than the chloronium and bromonium salts.

The fate of the aryl moiety cleaved from the arylhalonium salt was examined for the set of salts. Since the quantum yields of formation of the aryl radical product were weakly dependent on the concentration of the halonium salt, comparisons are made for 0.01 M solutions and are expressed as ratios to aryl halide, the corresponding cage-escape product (Table II). In direct photolysis of halonium salts, the relative yield of benzene increases from only 3.4% for the diphenylchloronium salt to 9% for the diphenylbromonium salt and to 20% for the diphenyliodonium salt. Similarly, in the bis(4-methylphenyl)halonium series, the relative toluene yield increased from 6.4% for the chloronium to 11% for the bromonium and

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Table III. Limiting Quantum Yields of Diarylhalonium Photolysis in Acetone, $\lambda = 300 \text{ nm}^a$

compd (Ar_2X^+ salt)	total	ArX	2-XBP	3-XBP	4-XBP	$k_q\tau$
$\text{Ph}_2\text{Cl}^+\text{PF}_6^-$	0.67	0.614	0.029	0.008	0.019	221 ± 17
$\text{Ph}_2\text{Br}^+\text{PF}_6^-$	0.55	0.454	0.074	0.012	0.0098	339 ± 23
$\text{Ph}_2\text{I}^+\text{Tf}^-$	0.50	0.393	0.076	0.0051	0.026	994 ± 15
4-Tol ₂ Cl ⁺ PF ₆ ⁻	0.69	0.648	0.023	0.023	-	884 ± 92
4-Tol ₂ Br ⁺ PF ₆ ⁻	0.60	0.528	0.046	0.021	-	724 ± 70
4-Tol ₂ I ⁺ PF ₆ ⁻	0.42	0.314	0.086	0.019	-	700 ± 130

^a 4-Tol = 4-methylphenyl; Ph = phenyl; XBP = halobiphenyl.

Table IV. Product Distribution of Halonium Salts, Irradiation at $\lambda = 248 \text{ nm}$ in Acetonitrile (Direct Photolysis) or $\lambda = 300 \text{ nm}$ in Acetone (Sensitized Photolysis)^a

compd	method	ratio of halogen products				ratio of recomb products		
		ArX	2-XBP	3-XBP	4-XBP	2-XBP	3-XBP	4-XBP
$\text{Ph}_2\text{Cl}^+\text{PF}_6^-$	direct	84	8	5	3	48	31	21
	sens	92	4	1	3	52	14	34
$\text{Ph}_2\text{Br}^+\text{PF}_6^-$	direct	81	9	6	4	51	30	19
	sens	83	13	2	2	77	13	10
$\text{Ph}_2\text{I}^+\text{PF}_6^-$	direct	74	19	3	4	73	13	15
	sens	79	15	1	5	71	5	24
4-Tol ₂ Cl ⁺ PF ₆ ⁻	direct	85	5	10	-	34	66	-
	sens	93	3	3	-	50	50	-
4-Tol ₂ Br ⁺ PF ₆ ⁻	direct	82	11	6	-	64	36	-
	sens	89	8	3	-	69	31	-
4-Tol ₂ I ⁺ PF ₆ ⁻	direct	71	23	6	-	79	21	-
	sens	75	21	5	-	82	18	-

^a XBP = halobiphenyl.

to 38% for the iodonium. Acetanilide was also found to be formed in these photolyses. The quantification of acetanilide was less precise than the quantification of the other volatile compounds, leading to relative errors of around 20%.²⁵ For diphenylchloronium hexafluorophosphate, the yield of acetanilide relative to chlorobenzene was 110%; for the diphenylbromonium salt, the ratio was 91%; and for iodobenzene, the ratio was 78%. Thus, within experimental error, the formation of benzene and acetanilide accounts for the fate of the escape phenyl moiety in the direct photolysis of the diarylhalonium salts in acetonitrile.

The sensitized decomposition of the diarylhalonium salts by acetone was also examined (Table III). Limiting quantum yields were obtained by a double reciprocal plot of the quantum yields at four concentrations of halonium salt (Figure 1). The Stern-Volmer slope $k_q\tau$ was obtained by taking the ratio of the intercept of the plot to the slope.²⁶ The limiting quantum yields upon triplet excitation were of the same order of magnitude as the direct photolysis quantum yields, although about 10–20% lower. The quantum yields decreased in the series chloronium, bromonium, and iodonium, by amounts similar to those of the direct photolysis. For diphenyliodonium triflate and the three bis(4-methylphenyl)halonium salts, the $k_q\tau$ values are roughly the same, from 700 to 1000. If the lifetime of the acetone triplet state is taken to be $0.9 \times 10^{-6} \text{ s}$, a quenching rate constant of about 10^9 s^{-1} is obtained.²⁷ This is about 10 times smaller than the diffusion-controlled rate constant and may be the result of competitive quenching by impurities such as residual oxygen or mesityl oxide. For diphenylchloronium and diphenylbromonium, however, the $k_q\tau$ value is significantly lower. This could

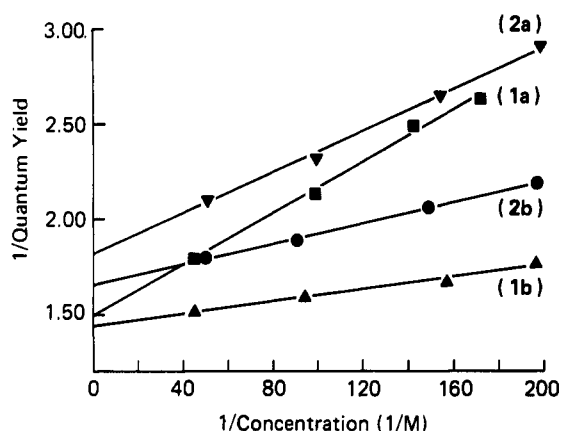


Figure 1. Double reciprocal plots, $1/\Phi$ versus $1/[\text{Ar}_2\text{X}^+\text{Y}^-]$, for triplet-sensitized photodecomposition of diarylchloronium and diarylbromonium salts, in acetone.

be due to the possible higher triplet energy of these compounds relative to diphenyliodonium and the ditolylhalonium salts, which would result in triplet energy transfer occurring at a rate somewhat less than that of diffusion.

The product distribution upon sensitized photolysis is shown in Table IV. The 2-halobiaryl is the major isomer in almost all photolyses. Going from chloronium to bromonium to iodonium, the amount of 2-halobiaryl isomer increases, and the amount of the 3-halobiaryl isomer decreases. The relative amount of the 4-halobiaryl isomer shows no clear trend. Benzene and toluene were also quantified for the 0.01 M solutions upon acetone sensitization (Table II). Relative to the other escape product, the haloarene, diphenylchloronium and diphenylbromonium salts gave a ratio of 93%, where in the case of the diphenyliodonium salt, the ratio was only 50%. The amount of toluene produced upon sensitization of the bis(4-methylphenyl)halonium salts increased from 50% for the chloronium to 83% for the bromonium and to 87% for the iodonium. These results show that the escape products upon sensitized photolysis are predominantly derived from a homolytic process.

(25) This problem was circumvented for triarylsulfonium salts by trapping the escape aryl cation with methanol to give anisole. Unfortunately, halonium salts undergo catalytic photoinitiated decomposition by a radical chain mechanism in methanol, preventing its use as an aryl cation trap.

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Discussion

The results of our investigation show that arylhalonium salts undergo efficient photochemistry to yield haloarenes, arene, and acetanilide as the major products in acetonitrile, along with recombination products. In our investigation, biphenyl was not found to be a significant primary photoproduct and formation of reduced arene is a minor process. Thus, for direct photolysis of the halonium salt, cleavage to give phenyl radical represents a relatively minor decomposition pathway. In contrast, acetanilide was found to be a significant product from direct photolysis of all the halonium salts. The presence of acetanilide usually implies the formation of phenyl cation by heterolysis of the excited onium salt and requires that the heterolysis mechanism be operating in competition with the previously postulated homolytic mechanism.⁷

Previous studies on the reactions of phenyl cation with chlorobenzene include β decay of tritioarene²⁸ and thermal decomposition of phenyldiazonium tetrafluoroborate and phenylazo *p*-tolyl sulfone.^{29,30} In each case chlorobiphenyl isomers were obtained. The product distribution of the isomeric chlorobiphenyls from the direct photolysis of diphenylchloronium salts also supports the intermediacy of phenyl cation. The product ratio of 2-, 3-, and 4-chloro(tritio)biphenyls occurring from 4-tritio-phenyl cation, formed by β decay of 1,4-ditritio-*benzene* in pure chlorobenzene, is 50:29:21.²⁸ This agrees well with our result of 48:31:21, for chlorobiphenyls (Table IV), obtained from the photochemical decomposition of diphenylchloronium salt. However, the distribution obtained for decomposition of the diazonium salt in acetonitrile/chlorobenzene solutions was found to be 61:15:24,²⁹ whereas thermolysis of the sulfone in neat chlorobenzene gave the ratio 71:8:21 and thermolysis of the sulfone in acetonitrile/chlorobenzene gave 51:19:30.³⁰ Zollinger has shown that the decomposition of diazonium salts in trifluoroethanol is a second-order reaction, depending on substrate concentration, and concluded that solvent or nucleophile participated in the loss of N₂ from the diazonium salt.^{31,32} Hence free phenyl cations were not an intermediate in the diazonium salt reactions. Our data is consistent with this view. We propose the formation of phenyl cation from the chloronium excited state in a rapid process, which should lead to a phenyl cation in a solvent cage, without nucleophilic assistance. The β decay experiment also produced a phenyl cation, without nucleophile involvement. The similarity of product distributions obtained from both the β decay reaction and photolysis of the chloronium salt implies a common intermediate, phenyl cation.

In contrast to the direct irradiation, the acetone-sensitized photolysis of arylhalonium salts apparently occurs by a homolytic cleavage. In almost all of the salts examined, the major aryl escape product appears as benzene or toluene. The distribution of the isomers of the recombination products, the halobiaryls, is also consistent with a radical process. While the direct irradiation of diphenylchloronium hexafluorophosphate gave a product ratio consistent with phenyl cation in chlorobenzene,²⁸ the sensitized reaction gave less of the 3-isomer and relatively more of the 4-isomer of chlorobiphenyl (Table IV). If phenyl radical were to attack chlorobenzene radical cation,

as we propose for the sensitized decomposition, the 2- and 4-positions should be preferentially attacked, as odd-electron density might be expected to be highest at these positions, due to the ability of the odd electron in these positions to delocalize onto chlorine. A similar trend is observed for the bromonium and iodonium salts.

It is noteworthy that recombination products (the halobiaryls) are obtained for both the direct and sensitized reactions. In our studies of triarylsulfonium salt photochemistry, we found that recombination products were only obtained upon direct irradiation, and not with sensitization by acetone,⁶⁻⁸ and in a later paper, we suggested that this difference in product formation between the sulfonium and iodonium salts might be related to enhanced intersystem crossing in the phenyl radical pair by either spin-orbit coupling ("heavy-atom effect") or spin-spin coupling of the odd-electron spin with the nuclear spin of the heteroatom.²¹ The spin-spin coupling mechanism has been previously proposed to account for trends seen in the photochemistry of benzylammonium, -phosphonium, and -arsonium salts.¹³ In the current study, the fraction of rearrangement products in the triplet-sensitized photolyses ranges from 7% in the case of bis(4-methylphenyl)chloronium hexafluorophosphate to 25% for bis(4-methylphenyl)iodonium hexafluorophosphate. The diphenylhalonium salts show a similar trend. To form recombination products, the initially formed triplet geminate radical pair must undergo intersystem crossing to form the singlet radical pair. It is unlikely that spin-orbit coupling is involved in this mechanism, as the relative amount of escape to recombination processes varies only by a factor of 4 for the three halogens investigated. However, the results of this study support the role of spin-spin coupling as a factor in the formation of the recombination products. The spin density on the halogen in the halobenzene radical cation, which is derived from the magnitude of the hyperfine coupling, increases in the series chlorine, bromine, and iodine.³³ Since the rate of intersystem crossing (isc) should be proportional to the magnitude of the hyperfine coupling,²⁶ this mechanism predicts that the highest isc rate should occur for the iodonium salts. In fact, the highest proportion of recombination products occurs upon triplet sensitization of the iodonium salts. However, since the hyperfine coupling constants do not vary greatly, the intersystem crossing rates should not vary greatly, leading to the formation of the singlet radical pair and thus recombination products for all of the halonium salts. However, for sulfur, for which the major natural isotope has no nuclear spin, this mechanism cannot occur.

A factor that might account for the amount of heterolytic cleavage versus homolytic cleavage upon direct irradiation of arylhalonium salts is the rate of intersystem crossing of the halonium singlet excited state to the triplet excited state. Spin-orbit coupling is the mechanism for this singlet-triplet conversion,²⁶ which means that the rate should be highest for the heaviest atom. One factor that might slow the rate of isc is that because the halonium salt is dicoordinate, one less lone-pair orbital is available over other halogen compounds (such as iodobenzene). For the rate of intersystem crossing to affect the products observed, a heterolytic cleavage from the singlet state and a homolytic cleavage from the triplet state would be necessary. Such state specificity of cleavage for a σ bond has been proposed, in general.²⁶ Thus, a heterolytic cleavage that forms an aryl cation would occur from the initial singlet excited state. In competition with this process, intersystem

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crossing would occur to form the halonium triplet excited state. This state would then cleave to produce the aryl radical-haloarene radical cation pair. Thus, for the iodonium salt compared with the chloronium salt, more radical products are expected, as is observed, due to the heavy atom accelerated rate of intersystem crossing.

We had previously concluded that a possible factor influencing the amount of heterolytic versus homolytic cleavage of the diaryliodonium and triarylsulfonium salts was thermodynamic stability of the initially formed pairs of intermediates.^{7,21} In Table II, the relevant data is presented for the halonium salts studied in this investigation. The half-wave oxidation potential for the aryl halides was obtained from the literature.^{34,35} Combined with an estimate of the oxidation potential of phenyl radical of 2.08 V,³⁶ an estimate can be made of the stability of the aryl cation-haloarene pair relative to the stability of the aryl radical-haloarene radical cation pair. It can be seen that, for the diphenyl series, the phenyl cation pair should be more stable for the diphenylchloronium and the diphenylbromonium salts and should be of comparable stability for the iodonium salt. In the bis(4-methylphenyl)halonium series, the comparison is not as facile, as the value for the ionization potential of the 4-methylphenyl radical does not appear to be known. The value for phenyl radical was used as an approximation to the 4-methylphenyl radical.³⁷ The values in Table II show that the intermediates in the photolysis of the tolylchloronium salt are predicted to be of comparable stability, as in the diphenyliodonium salt. The tolyl radical-bromotoluene radical cation pair is predicted to be somewhat more stable than the tolyl cation pair, and for the case of the tolyliodonium, the radical pair should certainly be more stable.

The predicted order of stability of the phenyl radical pair relative to the phenyl cation pair may rationalize the relative yields of homolytic and heterolytic products obtained in the direct photolysis. For the diphenylhalonium series, the chloronium and bromonium salts are predicted to have the intermediate phenyl cation pair be more stable, and only small amounts of benzene, the radical product, are obtained. The phenyl radical and phenyl cation pairs derived from the diphenyliodonium salt are predicted to be of comparable stability, and 20% of the phenyl moieties appear as benzene. A similar trend is apparent in the ditolyhalonium series. The diphenyl- and ditolyhalonium results do not compare well with each other. Since the diphenyliodonium and the bis(4-methylphenyl)chloronium salts are predicted to yield intermediate pairs of comparable stability, they might be expected to give similar relative yields of reduced arene. However, the ditolychloronium ratio of 6.4% falls in between the diphenylchloronium and the diphenylbromonium values. Thus, the ditolyhalonium data would be more consistent with the diphenylhalonium data if the calculated ΔG were lower by about 5 kcal mol⁻¹. This discrepancy might arise from the assumed equivalence of the 4-methylphenyl and phenyl

radical oxidation potentials and suggests that the 4-methylphenyl radical might be easier to oxidize by about 0.2 V.

The order of stability of the proposed intermediates may also be reflected in the product distributions and quantum yields. The diphenylchloronium and diphenylbromonium salts, upon direct irradiation, show a similar ratio of escape to recombination processes and similar quantum yields of decomposition. However, the diphenyliodonium shows a much lower ratio of escape to recombination, and a decomposition quantum yield 30% lower than those of the bromonium and chloronium salts. In addition, the distribution of the recombination products is similar for both the chloronium and bromonium salts. Relative to these salts, the recombination product distribution for the iodonium salt favors the ortho product at the expense primarily of the meta product, although the para product is formed in somewhat lower relative yield. These trends are consistent with the proposed order of stability of the intermediates. The diphenylchloronium and diphenylbromonium salts, in which the phenyl cation pair should have greater stability, show very similar chemistry. The "internal conversion" quantum yield, which is the difference between the decomposition quantum yield and unity, can be partially attributed to back-recombination of the phenyl cation and the halobenzene occurring at the halogen, to re-form starting halonium salt. The high ratios of escape to recombination can be explained, in that phenyl cation should react very rapidly with the solvent molecules in the solvent cage walls. In contrast, the diphenyliodonium salt shows different behavior. The internal conversion quantum yield increases by 230% relative to the values for bromonium and chloronium salts. The escape to recombination ratio decreases, and the position preference of the recombination products changes. These effects are best explained in that this reaction occurs at least partly through the phenyl radical pair. Phenyl radical is much less reactive than phenyl cation. The hydrogen abstraction rate constant would be expected to be of the order of 10⁵ s⁻¹,³⁸ implying that the cage lifetime of the phenyl radical pair might be longer than that of the phenyl cation pair. This results in more recombination relative to escape, primarily to re-form diphenyliodonium. The different recombination product distribution can be explained in that the phenyl radical and the iodobenzene radical cation should show a preference for recombination at the ortho and para positions and the iodine atom. The spin density on iodine for the iodobenzene radical cation has been estimated to be about 0.46 from ESR measurements of the hyperfine coupling.³³ The iodine can also stabilize the spin on the ortho and para positions, but not the meta position. It is unlikely that phenyl cation would show similar selectivity for the bromonium and chloronium salts, but not for the iodonium salt.

Intersystem crossing of the excited halonium salt and interconversion by electron transfer of the intermediate pairs are both feasible mechanistic pathways to explain the relative amounts of homolytic and heterolytic cleavage in the direct photolysis of arylhalonium salts. Each pathway accounts for the formation of heterolytic and homolytic products and for the trends observed with variation in halonium salt. Arguments can be made to support both alternatives. The intersystem crossing of the excited halonium salt would have to be very fast to compete with the cleavage reaction. The high quantum yield for this process can be interpreted as implying a fast rate

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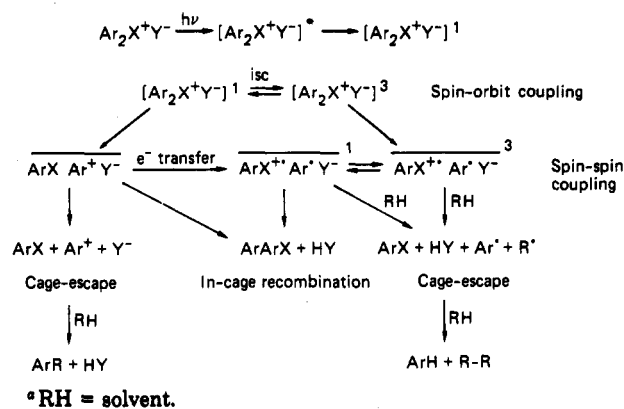
(37) This should give a reasonable estimate for the stability of the intermediate pairs because the methyl group might be expected to have a larger effect on the haloarene oxidation potential, where the methyl group can directly stabilize the positive charge, than in the aryl radical-aryl cation couple where a stabilizing influence would be limited to inductive effects. Regardless of this approximation, the order of stability for the series should be internally consistent.

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of cleavage, to compete with other processes deactivating the excited state. Intersystem crossing in aromatic iodine derivatives is known to be very fast, so at least for the iodonium salt, the formation of the triplet state is a feasible reaction. The intersystem crossing would be slower for the bromonium and slower still for the chloronium, which would be consistent with the experimental evidence, assuming the specific hetero- or homolytic cleavage of the singlet and triplet states. The second possibility is that the trends observed upon direct irradiation are a result of the interconversion by electron transfer of the phenyl cation pair and the phenyl radical pair of intermediates. This possibility is somewhat less likely than the intersystem crossing explanation. Phenyl cation is known to be highly reactive with nucleophiles, as evidenced in this study by the formation of acetanilide, from attack of phenyl cation on the poor nucleophile acetonitrile. This implies that the corresponding aryl cation-haloarene pair would have a short lifetime, which might not permit the proposed electron transfer to kinetically compete with the cage-escape and recombination reactions. Although electron-transfer reactions can be very fast, several factors in the present case might retard this rate. There is a significant change in the calculated geometry between phenyl radical and singlet phenyl cation,³⁶ in that the carbon bearing the empty p orbital in phenyl cation attempts to attain the preferred linear geometry associated with vinyl cations. This would result in a low Franck-Condon factor for the ionization of phenyl radical. The lowest energy transition in the photoelectron spectrum of phenyl radical has thus been attributed to ionization to triplet phenyl cation, the first excited state, which would presumably have a geometry more similar to that of phenyl radical. The other factor that would retard the rate of electron transfer would be the low thermodynamic driving force, which would, in the Marcus treatment, result in a lower rate of electron transfer.³⁹ It would be difficult to assess the solvent reorganization energy, as in this case no large dipole is being created in the electron transfer, only a reorientation of a preexisting dipole. Thus, for the electron-transfer interconversion to be a workable mechanism in the direct photolysis of the arylhalonium salts, the electron-transfer rate would have to be competitive with the reaction rate of the aryl cation.

Upon triplet sensitization, the ratio of the radical escape product (benzene or toluene) to the total escape product as quantified as haloarene shows interesting behavior. For the bis(4-methylphenyl)halonium series, the fraction of radical escape products correlates with the trend in the relative stability of the aryl cation-haloarene pair against that of the aryl radical-haloarene radical cation pair. However, the diphenylhalonium series shows no such correlation. An explanation for this behavior may lie in the reactivity of the first formed radical pair with solvent or species outside of the radical cage. Within the diphenyl or ditolyl series, the same aryl radical is present in the cage, and no change in reactivity within the halonium series can be attributed to this fragment. Thus, the difference in reactivity of the radical pair can be attributed to the haloarene radical cation fragment. Since the precise reactions of the haloarene radical cation with solvent are not known, a rigorous measure of reactivity is not possible. However, the ability of these radical cations to function in one type of reaction, oxidation, is indicated by the redox potentials of the haloarene-haloarene radical cation couples. The data in Table II show that the chlorobenzene

Scheme III. Mechanism for Product Formation from Direct Photolysis of Diarylhalonium Salts^a

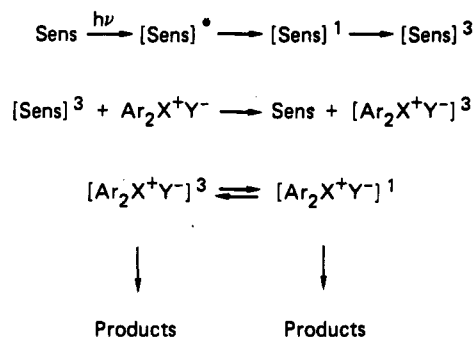


and bromobenzene radical cations are the strongest oxidants and thus potentially more reactive than the other radical cations, if this decrease in stability is correlated with greater reactivity for these species. This may explain why, even though the chlorobenzene-phenyl cation pair is calculated to be more stable, and singlet chlorobenzene radical cation-phenyl radical pair is formed from the evidence of recombination products, almost all products in the triplet-sensitized photolysis are radical derived. This stands in contrast to the bis(4-methylphenyl)chloronium salt, in which only 50% of the tolyl escape moieties are radical derived. This difference is thus explained in that the chlorobenzene radical cation-phenyl radical pair has too short a lifetime for the electron transfer to form the phenyl cation pair to compete with other reactions leading to escape products. If the 4-chlorotoluene radical cation-4-tolyl radical pair has a longer lifetime (is less reactive), then the electron transfer to form the 4-tolyl cation pair might compete. This accounts for the correlation between the stability of the intermediate pairs and the fraction of radical products for the tolyl series and for the lack of correlation in the diphenyl series.

Conclusions

This investigation into the direct and sensitized photochemistry of arylhalonium salts has resulted in a clearer picture of how these salts decompose photochemically. As shown in Scheme III, upon direct irradiation of an arylhalonium salt, the singlet excited state is formed. This may undergo heterolytic cleavage to form the aryl cation-haloarene pair, or it may undergo intersystem crossing to form the triplet excited state. The triplet excited state would undergo either internal conversion to the ground state or homolysis to the triplet aryl radical-haloarene pair. The triplet excited state can also be formed by triplet sensitization using high-energy sensitizers (Scheme IV). The intermediate pairs may then undergo reactions. The triplet aryl radical pair undergoes cage-escape reactions or intersystem crossing to the singlet radical pair, a process mediated by the spin-spin coupling between the haloarene radical cation odd electron and the nuclear spin of the halogen. The singlet radical pair then might undergo electron transfer to form the aryl cation pair of intermediates, and it is possible that the aryl cation pair might undergo the reverse process. The products observed are then derived from the intermediate pairs. Solvent addition products like acetanilide are formed from the aryl cation and produce haloarene as the corresponding product. Aryl radical can abstract hydrogen from the environment and produce reduced arene as product. The corresponding haloarene radical cation would then be reduced by the

Scheme IV. Mechanism for Sensitization of Diarylhalonium Salts by Triplet Energy Transfer



environment to form the haloarene, although the mechanism of this process is not clear. The halobiaryls are formed either by electrophilic attack of aryl cation on the cage-partner haloarene or by radical recombination of the aryl radical on its cage partner, the haloarene radical cation. The intermediate cyclohexadienyl cations then lose a proton to the environment. This study has also demonstrated that the trends observed in the efficiencies and product distributions can be related to stabilities of the proposed intermediates and to interaction of the halogen nuclear spin with the free-radical intermediates.

Experimental Section

For general information, see ref 7. 2-Bromobiphenyl and 3-bromobiphenyl were obtained from Columbia Organics; 2-, 3-, and 4-chlorobiphenyl were obtained from Lancaster Synthesis. All other chemicals were obtained from Aldrich Chemical Co. For preparation of the iodonium salts and sources for iodide photo-products, see ref 21.

General Procedure for Halonium Salt Synthesis. A modification of the procedure of Olah et al. was used, and all ^{13}C NMR chemical shifts agreed well with those previously reported.²⁴ The structures of the salts were also confirmed by ^1H NMR and IR spectroscopy. The preparation of bis(4-methylphenyl)-bromonium hexafluorophosphate is a representative procedure. A 26-g portion of dry 4-methylbenzenediazonium hexafluorophosphate was mixed with a 60-mL portion of 4-bromotoluene and a 30-mL portion of trifluoroacetic acid. The mixture was heated slowly with a water bath to 70 °C, and the reaction mixture evolved copious fumes (N_2 and PF_5). After 2 h of stirring at 70 °C, the mixture was cooled, 100 mL of 1:1 hexane-ether was added, and the mixture was extracted with three 150-mL portions of water. The combined water extracts were treated with a 7-mL

portion of 60% hexafluorophosphoric acid, upon addition of which a precipitate developed. After 0.5 h of stirring, the precipitate became more crystalline and was collected by suction filtration. The solid was dissolved in the minimum amount of acetone and filtered, and ether was added to the filtrate. The bis(4-methylphenyl)bromonium hexafluorophosphate salt precipitated, the crystals were collected by filtration, and the solvent was removed in a vacuum oven at ambient temperature overnight, to give 1.28 g of salt, 3.2%: UV λ_{max} 234 nm ($17\,400\ \text{M}^{-1}\ \text{cm}^{-1}$); IR (KBr pellet) 845, 558, 804, 993, 1479, 697, 1188, 1492, 1453, 1005, 780, 1210 cm^{-1} ; ^1H NMR (acetone- d_6) δ 8.14 (d, 4 H), 7.53 (d, 4 H), 2.42 (s, 6 H) ppm; ^{13}C NMR (acetone- d_6) δ 145.8, 134.2, 131.8, 131.0, 21.2 ppm.

In a similar fashion, the following salts were prepared.

Diphenylchloronium hexafluorophosphate: UV λ_{max} 222 ($13\,300\ \text{M}^{-1}\ \text{cm}^{-1}$), 264 nm (2000).

Bis(4-methylphenyl)chloronium hexafluorophosphate: UV λ_{max} 232 nm ($16\,500\ \text{M}^{-1}\ \text{cm}^{-1}$).

Diphenylbromonium hexafluorophosphate: UV λ_{max} 224 nm ($14\,800\ \text{M}^{-1}\ \text{cm}^{-1}$).

Preparation of the Halobiaryls. The organic extracts from the onium salt formation reaction were extracted with 50 mL of 5% sodium hydroxide solution and with 50 mL of brine. The organic layer was dried with magnesium sulfate, the solvents were removed by using a rotary evaporator, and the residue was distilled under vacuum (about 1 Torr) to remove all of the lower boiling material. The pot residue was then separated by preparative GLC; Shimadzu GC-8, temperature program 230–260 °C at 3 deg/min. The column used was 0.25 in. \times 10 ft 5% SE-30 on Chromosorb G, AW-DMCS, 60–80 mesh.

2-Bromo-4',5'-dimethylbiphenyl: ^1H NMR (chloroform- d) δ 7.53–6.97 (m, 7 H), 2.40 (s, 3 H), 2.33 (s, 3 H) ppm.

5-Bromo-2,4'-dimethylbiphenyl: ^1H NMR (chloroform- d) δ 7.52–6.96 (m, 7 H), 2.40 (s, 3 H), 2.20 (s, 3 H) ppm.

2-Chloro-4',5'-dimethylbiphenyl: ^1H NMR (chloroform- d) δ 7.35–7.05 (m, 7 H), 2.41 (s, 3 H), 2.35 (s, 3 H).

5-Chloro-2,4'-dimethylbiphenyl: ^1H NMR (chloroform- d) δ 7.35–7.19 (m, 7 H), 2.40 (s, 3 H), 2.22 (s, 3 H).

Quantum Yields. Samples were irradiated in a PTI Quantacount apparatus, which was calibrated by using potassium ferrioxalate actinometry.⁴⁰ The photoproducts were then analyzed by GLC.^{7,21} Because of the thermal lability of the chloronium and bromonium salts, two unirradiated aliquots were analyzed by GLC to account for any partial decomposition (usually found to be less than 0.5%).

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