Heteroatom Chemistry
Volume 7, Number 5, 1996

Acid Generation in the Thermal Decomposition of Diaryliodonium Salts

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Received 28 March 1996; revised 12 May 1996

ABSTRACT

Diphenyliodonium tetrafluoroborate and diphenyliodonium hexafluorophosphate have been found to generate up to two equivalents of hydrogen fluoride per equivalent of the iodonium salt by pyrolysis at 239°C in the neat state and at 150°C in the presence of anisole or nitrobenzene. The formation of hydrogen fluoride is presumed to arise by dissociation of hydrogen tetrafluoroborate or hydrogen hexafluorophosphate initially formed, due to the high temperatures, thus giving rise also to the Lewis acids boron trifluoride and phosphorus pentafluoride, respectively. A detailed analysis of the volatile organic products of the decomposition of the diphenyliodonium salts was also carried out. Many products were identified in all of the cases studied. For example, the neat decomposition of diphenyliodonium tetrafluoroborate afforded benzene, fluorobenzene, iodobenzene, the three isomeric iodobiphenyls, biphenyl, three isomeric terphenyls, and one or more of the diiodobiphenyls, iodoterphenyls, and polyaromatics. Among the iodobiphenyls, the ortho and para isomers were found to predominate over the meta isomer. The terphenyl isomers did not exhibit this ortho, para selectivity. It was significant that decomposition of the diaryliodonium salts in anisole suspension did not afford methoxybiphenyls or iodomethoxybiphenyls. An interpretation of these results is presented. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The photochemistry of diphenyliodonium salts in alcohol solutions was originally studied by Knapczyk et al. [1]. Although the mechanism of the reaction originally proposed by these workers still remains valid in its essential regards, Dektar and co-workers [2,3] have recently undertaken much more extensive studies of this and related reactions due to a remarkable increase in the applications of such salts as photoinitiators of acid-catalyzed reactions in polymer systems of industrial importance. Applications of the use of such salts in the design of both positive and negative photoresists, originally by Crivello [4], have led to explosive growth of the use of this chemistry in the electronics industry. Additional sophistication in the use of this chemistry by the development of a concept known as chemical amplification was provided by MacDonald et al. [5]. With regard to the fundamental chemistry, it is now generally believed that diphenyliodonium salts with non-nucleophilic anions form photolysis products by both homolysis to a phenyl radical plus an iodobenzene radical cation and also heterolysis to a phenyl cation plus iodobenzene, with interconversion of the initially formed high-energy intermediates taking place by a process of electron transfer [2,3]. The iodobenzene radical cation abstracts a hydrogen atom from a suitable substrate (usually the solvent) to produce iodobenzene and a strong Lewis acid.

It is almost a watchword of the practitioners of photoimaging technology that an important facet of the success of diphenyliodonium salts as photoacid generators lies in their thermal stability, as against

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Dedicated to Professor Louis D. Quin, a good friend and distinguished colleague, on the occasion of his retirement from the University of Massachusetts at Amherst.

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1042-7163/96/050349-06

their high photochemical reactivity to produce "instant acid." However, it is well known that most organic compounds have some degree of thermodynamic instability and will undergo decomposition at a sufficiently high temperature. As applied to the use of diphenyliodonium salts in microprocessor design, this could be of importance since the resist materials are generally subjected at some stage to a baking process. With this in mind, we have undertaken a detailed examination of the thermolysis reaction of diphenyliodonium tetrafluoroborate, in particular.

RESULTS AND DISCUSSION

To determine whether strong Bronsted acids can be obtained by thermolysis of diphenyliodonium salts, the tetrafluoroborate and hexafluorophosphate salts were subjected to neat pyrolysis at 239°C. Also, the fluoroborate salt was heated to 150°C in anisole and nitrobenzene solutions. To determine the amounts of acid generated, simple titrations were carried out. Quantitative ion chromatography was used to determine the amount and the identities of the ions present. The results are summarized in Table 1. The amounts of acid generated were found to be the greatest in the neat decompositions, with the hexafluorophosphate salt generating the most acid (up to 2.1 equivalents of acid per equivalent of salt). The amount of acid generated was found to decrease in the presence of anisole or nitrobenzene at the lower temperature (0.6–0.9 equivalent of acid being produced per equivalent of salt). Ion chromatography revealed two acids to be present in the case of the decomposition of diphenyliodonium hexafluorophosphate, viz., hydrofluoric and phosphoric acids. The composition was found to be 96% hydrofluoric acid and 4% phosphoric acid. Because of the small quantity of phosphoric acid, a titration curve resembling that for the neutralization of a strong monoprotic acid was obtained, with but little indication of the presence of phosphoric acid. It is of interest that, in the neat decompositions, larger amounts of fluorobenzene and polyaromatic compounds were found than in the decompositions carried out in the presence of anisole or nitrobenzene (vide infra). The origin of the protons of the hydrofluoric acid in these pyrolysis reactions is complex. The generation of protons is largely the result of coupling and substitution reactions of reactive aryl entities, with subsequent aromatizations (vide infra). The protons presumably react with the tetrafluoroborate and hexafluorophosphate anions at the elevated temperatures to form HF and boron trifluoride (bp − 126°C) and phosphorus pentafluoride (bp − 84.6°C), respectively, these Lewis acids mainly escaping as volatile gases when the sealed reaction vessels are opened. A small amount of phosphorus pentafluoride is hydrolyzed to give phosphoric acid and some additional hydrofluoric acid when the contents of the vessels are added to water.

There are many examples of the thermal decomposition of diaryliodonium salts in the literature [6–14], but, with the exception of work carried out in an aqueous medium [14], none dealt with the subject of acid generation. Our work was specifically designed to investigate the detailed chemistry leading to the formation of Bronsted acids in the pyrolysis of diphenyliodonium salts. By use of gas chromatography mass spectroscopy (GCMS) techniques, we determined that a large number of organic products were produced in the pyrolysis reactions. For example, diphenyliodonium tetrafluoroborate produced benzene; fluorobenzene; iodobenzene; the three iodobiphenyl isomers; biphenyl; the three terphenyl isomers; and one or more diiodobenzenes, diiodobiphenyls, iodoterphenyls, and higher polyaromatics when pyrolyzed. Among the iodobiphenyls, the ortho and para isomers were found to predominate over the meta isomer. On the other hand, the terphenyl isomers were found to lack this type of selectivity (Table 2).

The terphenyls and biphenyl have tentatively

TABLE 1 Acid Generated by the Thermal Decomposition of Diphenyliodonium Salts

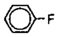
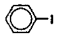
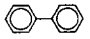
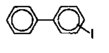
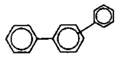
					Number of Equivalents[a]		
Entry	*mg*	*Temp (°C)*	*Additives*	*Counter Ion*	*Trial 1*	*Trial 2*	*Trial 3*
1	117	150	anisole	1[b]	0.88	0.78	—
2	101	150	nitrobenzene	1[b]	0.63	0.58	—
3	104	250	—	1[b]	1.89	1.92	2.10
4	105	250	—	2[c]	1.34	1.38	—
5	137	250	KF	2[c]	0.93	0.92	—

[a] Based on starting material.

[b] PF_6^-.

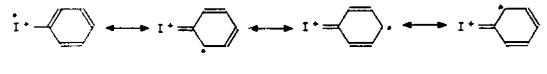
[c] BF_4^-.

TABLE 2 Mole % of Volatile Products from the Decomposition of Diphenyliodonium Tetrafluoroborate

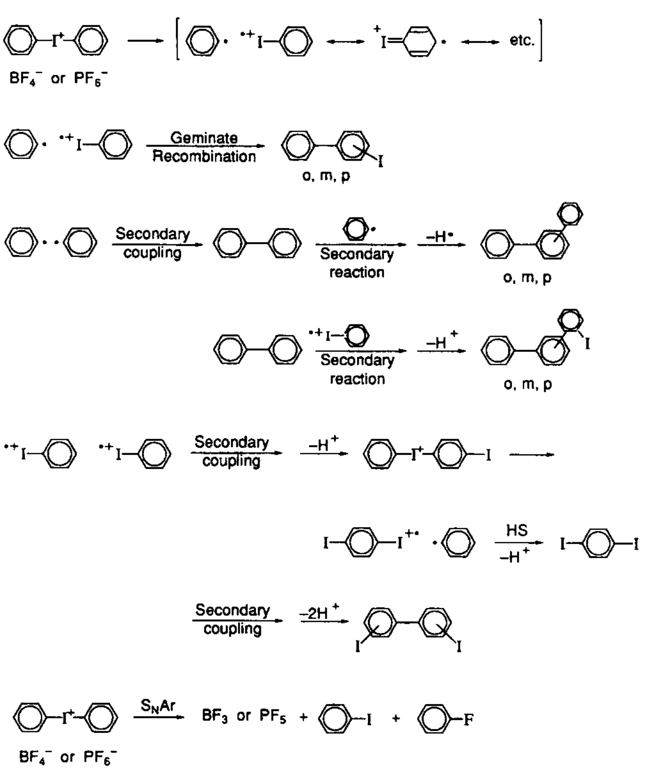
Solvent	*Counter Ion*						
						o, m, p	o, m, p
—	BF_4^-	0.082	16.979	62.603	4.875	4.022, 1.081, 4.496	1.366, 1.650, 2.846
Anisole	BF_4^-	trace	1.174	85.251	3.523	3.288, 1.010, 5.049	0.468 – 0.235
Nitrobenzene	BF_4^-	trace	2.003	84.278	2.381	3.968, 1.058, 5.253	0.680 – 0.378

been classified as products derived from reactions involving clusters contained in a cage, while the iodobiphenyls are considered to be products of geminate in-cage recombination. In the strict use of the term "cage," a solvent must be present to restrict the reagents to a confined "place" where a higher frequency of collisions can occur among the molecules of the reagents. A solvent is obviously absent in the case of a neat decomposition; thus, the conventional use of the term "cage" does not apply. However, unreacted diphenyliodonium salt molecules encountered in the early molten solution might serve to contain the dissociated radical fragments, thus acting as a de facto solvent cage. Therefore, the designation of "in-cage" products seems to be acceptable, since the fragments resulting from C–I bond cleavage may remain together and form geminate recombination products. Concomitantly, some of the reactive radicals may attack newly formed intermediates produced in the cluster. This is not the same process as that which occurs when radicals diffuse from a cage to form products by reactions with other molecules, e.g., solvent molecules.

A comprehensive mechanistic scheme accounting for all of the products, including both the formation of reactive free-radical intermediates and their subsequent reactions and a competing aromatic nucleophilic substitution reaction to account for the formation of fluorobenzene, is shown in Scheme 1. Fluorobenzene is considered to be formed by an S_NAr reaction in which a fluoride ion attacks the diphenyliodonium ion with eventual departure of iodobenzene. This competes with homolytic cleavage of the C–I bond of the ion that gives rise to the iodobenzene radical cation and the phenyl radical. These radicals can undergo geminate coupling, with subsequent loss of a proton, to form the iodobiphenyl isomers. The iodobenzene radical cation can be depicted in terms of the canonical structures



Geminate coupling of this radical cation with the phenyl radical in the cage preferentially yields the ortho and para isomers of the iodobiphenyls (after loss of a proton) because the radical character resides at the ortho and para carbon atoms to a greater degree than at the meta carbon atom. It should also be noted that the two major transition intermediates formed by the geminate coupling of the iodobenzene radical cation with the phenyl radical resemble arenium ions. These unstable intermediates may combine with another phenyl radical or iodobenzene radical cation to form, eventually, iodoterphenyls and diiodoterphenyls, respectively, which have been detected in trace amounts. Also, iodoterphenyls may



SCHEME 1 Proposed mechanism for the thermal decomposition of diphenyliodonium tetrafluoroborate.

be formed by attack of the iodobenzene radical cation on biphenyl, in a secondary reaction, with subsequent loss of a proton. Reutov and Ertel [12] reported that iodobenzene containing I^{131} became incorporated into an unlabeled diphenyliodonium salt on pyrolysis of a mixture of the two compounds. Although a mechanism for this exchange reaction was not proposed by Reutov and Ertel, we suggest that the labeled diphenyliodonium salt was formed by an initial homolytic cleavage of the unlabeled diphenyliodonium cation to the iodobenzene radical cation and phenyl radical, followed by an electron transfer between labeled iodobenzene and the unlabeled iodobenzene radical cation to form the labeled radical cation, which then combined with the phenyl radical to give, eventually, the labeled diphenyliodonium cation (Scheme 2). This offers support for the general mechanistic scheme that we have proposed.

Another pathway that should be considered, in view of the work of Dektar and co-workers [2,3], is the initial thermal cleavage of the C–I bond of the diphenyliodonium cation to form iodobenzene and a phenyl cation. A cage electrophilic substitution reaction involving these intermediates could have produced iodobiphenyls, mainly ortho and para, but *m*-iodobiphenyl should not have been formed in any but a very small amount. Also, the phenyl cation could have been captured by any available nucleophile, since it is a highly reactive electrophile. On the basis of the results presented in Table 2, this possible mechanistic pathway seems to be unlikely. Two observations diminish the possibility of this heterolytic reaction path: (1) *m*-iodobiphenyl was actually produced in a substantial amount relative to the *o*,*p*-isomers, and (2) products of phenyl cation reactions were not found when the pyrolysis was carried out in an anisole suspension. No methoxybiphenyls were detected, and the yield of fluorobenzene was sharply reduced, which also provides an argument against the formation of the latter compound by an S_N1 process. Of course, the lower reaction temperature of the reaction with anisole present possibly also influences these results in some presently unknown way.

$$(C_6H_5)_2I^+ \longrightarrow C_6H_5I^{+\bullet} + C_6H_5^{\bullet}$$

$$C_6H_5I^{131} + C_6H_5I^{+\bullet} \xrightarrow{et} C_6H_5I^{131\bullet +} + C_6H_5I$$

$$C_6H_5I^{131\bullet +} + C_6H_5^{\bullet} \longrightarrow (C_6H_5)_2I^{131+}$$

SCHEME 2 Proposed mechanism for the incorporation of labeled iodobenzene into the diphenyliodonium cation (this being an interpretation of Reutov's data).

Dektar and co-workers [2,3] proposed that both pairs of reactive intermediates, the phenyl radical plus the iodobenzene radical cation, and the phenyl cation plus iodobenzene, are formed on photolysis of diphenyliodonium cations having non-nucleophilic anions. Furthermore, interconversion of these pairs of intermediates was proposed to occur by an electron-transfer process. Indeed, it is clear that the photolytic production of iodobiphenyls differs from the pyrolytic production of these compounds because the ratio of the isomers differs in the two procedures. Two possible explanations can be offered to explain the difference between our results and those of Dektar and co-workers: (1) The electron transfer between the pairs of reactive intermediates is a photochemical process, not a thermal one, and (2) the phenyl radical and iodobenzene radical cation are formed at a much higher energy level in the photochemical process than in the thermal process, and, at the higher energy level, the initial photolysis pair can undergo an electron-transfer process to form the phenyl cation plus iodobenzene. Of course, the exclusion of all but in-cage reactions would also account for the failure of methoxybiphenyls to be formed. The same could hold true for the failure of iodomethoxybiphenyls to be formed by reaction of the iodobenzene radical cation with anisole. Likewise, the same explanation could be offered to explain the absence of iodonitrobiphenyls resulting from radical attack of the iodobenzene radical cation on nitrobenzene when the latter is present.

It is of importance to define several terms involved in the discussion of thermoacid- (analogous to photoacid) generating properties of diaryliodonium salts. As shown in Scheme 1, the initial reaction of the pyrolysis of the diphenyliodonium cation is the formation of a geminate pair of radicals, the phenyl radical and the iodobenzene radical cation. The composition of the eventual products indicates that the initial geminate pair of radicals may undergo concomitant recombination and separation by diffusion. Recombination leads to the starting material and also to the eventual formation of the iodobiphenyl isomers, while the migration of the radicals within the domain of the ion pair aggregates leads to the formation of secondary coupling products and also to secondary reactions. Secondary coupling is the combining of two radicals that were not the constituents of the original geminate pair, such as the coupling of two phenyl radicals to form biphenyl or the coupling of two iodobenzene radical cations to form (after loss of two protons) the isomeric diiodobiphenyls. A secondary reaction is the attack of a radical on a compound confined within the ion pair aggregate, such as the reaction of a

TABLE 3 GCMS Results on the Products from the Decomposition of Diphenyliodonium Tetrafluoroborate

Entry	*Parent Ion/Base Ion/Other Ions*	*Identified with an Authentic Sample*	*Compound*
1	78	yes	benzene
2	96, M-acetylene = 70	yes	fluorobenzene
3	204, M-1 = 77	yes	iodobenzene
4	154, 154, M-acetylene = 128	yes	biphenyl
5	280, 280, M-1 = 152	yes	iodobiphenyl (o, m, p)
6	230, 230, M-acetylene = 202	yes	terphenyl (o, m, p)
7	330, 330, M-1 = 203	no	diiodobenzene
8	406, 406, M-21 = 152	no	diiodobiphenyl
9	356, 356, M-1 = 229	no	iodoterphenyl
10	326, 326	no	a polyaromatic

phenyl radical with biphenyl to form, after removal of a hydrogen atom from the transition intermediate, a terphenyl. Another example of a secondary reaction is the attack of an iodobenzene radical cation on biphenyl to afford, after loss of a proton from the intermediate transition ion, an iodoterphenyl. The generation of a proton in this case is self-evident. When a hydrogen atom is removed from the transition intermediate of an attack of a phenyl radical on a neutral molecule, such as biphenyl, another proton (i.e., a Bronsted acid) is produced if it is an iodobenzene radical cation that abstracts the hydrogen atom, thus forming the conjugate acid of iodobenzene, obviously a strong Bronsted acid, as well as the terphenyl. Reaction sequences such as these are the main sources of Bronsted acids in these thermoacid-generating reactions of diphenyliodonium salts.

The ability of triarylsulfonim salts having nonnucleophilic anions to function as photoacid-generating compounds was first reported by Knapczyk and McEwen [15]. These reagents are now of even wider use in a multitude of industrial applications than are diarlyiodonium salts. Therefore, we have carried out preliminary experiments to find out whether such salts are also thermoacid generators. They do indeed produce Bronsted acids when pyrolyzed, and we will report the results at some future time.

EXPERIMENTAL

Acid Generation by Neat Pyrolysis

A carefully weighed sample of diphenyliodonium salt, about 100 mg, was sealed in a capillary tube and heated at 250°C for 20 minutes. The cooled tube was opened and the contents added to a mixture of water and methylene chloride. The aqueous layer, after several extractions with methylene chloride, was diluted to 100 mL, and an aliquot was taken and titrated with standard (0.025 M) sodium hydroxide solution. These solutions were also measured for their specific ion content by use of ion chromatography. The results are summarized in Table 1.

Acid Generation by Thermolysis in the Presence of Anisole or Nitrobenzene

The diphenyliodonium salt was mixed with 1 mL of solvent, sealed in a small round-bottom flask, and heated at 150°C for 40 minutes. The cooled contents were treated in the same manner as described for the neat decomposition.

Neat Decompositions

A carefully weighed amount (about 50 mg) of the diphenyliodonium salt was sealed in a capillary tube and heated at 239°C for 15 minutes. The tube was opened and immediately treated with a measured amount of acetone to insure homogeneity of the measured sample that was injected into the GCMS instrument [HPGC5890 series mass selective detector (MSD)]. Column: 25M HPS, 0.12 id, 0.17 micron film. For comparison, samples of the major products were dissolved in measured amounts of acetone, and serial dilutions were effected ranging from 0.01% to 10% (v/v). Area response curves were prepared by plotting concentration against the ion current of the analytical samples. These curves were used to determine the number of moles present for each component of the reaction sample. The data of Table 2 provide the mole ratios of the major products. Mass spectra were obtained for each component of the reaction mixture and compared to the results of an authentic sample or a literature source. Typical data are shown in Table 3, which also provides the basis of the identification of the products formed in very small amounts.

Thermolyses in Solvents

Weighed samples of the diphenyliodonium salt (about 50 mg) and 15 μL of anisole or nitrobenzene were sealed in capillary tubes and heated at 150°C for 40 minutes. The workup and analyses were the same as described for the neat reaction products.

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