

Radiolysis of Solutions of Diphenyliodonium and Triphenylsulfonium Hexafluorophosphates in Various Solvents

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The radiolysis of solutions of Ph_2IPF_6 and Ph_3SPF_6 was undertaken in various kinds of solvents such as alcohols, ethers, acetone, acetonitrile, and dichloromethane. The salts decompose through one-electron reduction in all of the solvents except dichloromethane. The α -hydroxyalkyl and α -alkoxyalkyl radicals derived from the oxygen-containing solvents are oxidized by Ph_2IPF_6 to initiate a chain reaction. The kinetic chain length depends on the oxidation potentials of the radicals. In dichloromethane, which is an electron scavenger, the decomposition of the salts is much less pronounced than in the other solvents.

Introduction

Recently, there has been a growing interest in the application of diaryliodonium and triarylsulfonium salts with complex metal halide anions as photoinitiators for cationic polymerization.¹⁻¹⁸ Upon irradiation with UV light, the salts undergo photodecomposition to yield Brønsted acids capable of initiating cationic polymerization. In the preceding paper, we have reported on the radiation-induced cationic polymerization of tetrahydrofuran (THF) by Ph_2IPF_6 and Ph_3SPF_6 .¹⁹ When dilute THF solutions of the salts are irradiated with γ -rays, the salts decompose through one-electron reduction by the solvated electron. The electron scavenging by the salts results in prevention of neutralization of the radiolytically produced cation, $\text{THF}(\text{H}^+)$, which initiates the polymerization of THF. The rate of the polymerization with Ph_2IPF_6 is much higher than that with Ph_3SPF_6 , suggesting that the former salt provides the initiating cation by a chain reaction.

Numerous studies have been undertaken on the photochemical^{1-5,9-12,20-27} and electrochemical²⁸⁻³⁷ decomposi-

Table I. Yields of Decomposition Products in the Radiolysis of Solutions of Ph_2IPF_6 and Ph_3SPF_6 in Various Solvents at 0 °C^a

solvent	PhI from Ph_2IPF_6			Ph ₂ S from Ph_3SPF_6		
	irradn time, min	convn, %	G	irradn time, min	convn, %	G
methanol	3	100	b	20	3.7	2.5
THF	10	46	74 ^b	20	3.2	2.1
1,2-dimethoxyethane	10	21	28	20	4.4	3.0
1,4-dioxane	10	23	26	c	c	c
acetone	20	17	12	20	1.6	1.1
acetonitrile	20	4.1	3.1	20	3.2	2.3
dichloromethane	60	6.6	1.0	60	1.2	0.2

^aThe dose rate and the salt concentration were $5 \times 10^3 \text{ Gy h}^{-1}$ and $1 \times 10^{-2} \text{ mol dm}^{-3}$, respectively. ^bThe G(PhI) values determined at lower dose rates were 1.8×10^3 and 2.2×10^2 in methanol and THF, respectively (see text). ^cNot examined because of the low solubility of Ph_3SPF_6 in 1,4-dioxane.

tion of diaryliodonium salts and of various sulfonium salts involving those with alkyl substituents.³⁸ The electrochemical reduction of the iodonium and sulfonium salts results in carbon-iodine and carbon-sulfur σ -bond cleavages, respectively, as well as the photoexcitation of the

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salts. The occurrence of a chain reaction has been reported for the photochemical decomposition of the diphenyliodonium salts in ethanol, 2-propanol, and mixed THF-acetonitrile and 2-propanol-acetonitrile solutions.^{12,21} The propagation steps involve the oxidation of the radicals derived from the alcohols and THF. In this paper, we report a study of the radiolysis of solutions of Ph_2IPF_6 and Ph_3SPF_6 in various solvents such as alcohols, ethers, acetone, acetonitrile, and dichloromethane. Solvent dependence of the radiolysis is described.

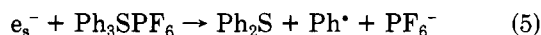
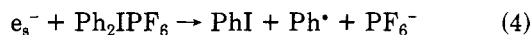
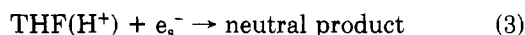
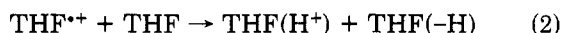
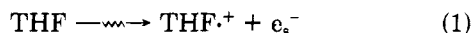
Experimental Section

THF, Ph_2IPF_6 , and Ph_3SPF_6 were the same as those used in the previous study.¹⁹ Methanol, ethanol, 2-propanol, acetone, 1,2-dimethoxyethane, and acetonitrile were fractionally distilled. 1,4-Dioxane was refluxed with aqueous hydrochloric acid, a slow stream of nitrogen being passed in through the condenser. After neutralization and drying with solid potassium hydroxide, it was distilled over sodium. Dichloromethane was washed three times with an aqueous solution of sodium hydroxide and water and then distilled over calcium hydroxide. The purified solvents were stored under vacuum over 3A molecular sieves, which had been baked at about 350 °C for several hours.

Details of sample preparation and procedures of the product analysis and pulse radiolysis experiments have been described in the previous paper.¹⁹

Results and Discussion

The primary processes and the one-electron reduction of Ph_2IPF_6 and Ph_3SPF_6 occurring in the irradiated THF solutions are represented as follows:



In this study the yields of the radiolysis products, PhI from Ph_2IPF_6 and Ph_2S from Ph_3SPF_6 , were determined in various solvents. The radiolysis was carried out at a salt concentration of $1 \times 10^{-2} \text{ mol dm}^{-3}$ at 0 °C.

The product yields at a dose rate of $5 \times 10^3 \text{ Gy h}^{-1}$ are presented in Table I. The yield of PhI from Ph_2IPF_6 is highest in methanol; the 100% yield is obtained by the 3-min irradiation. It is smallest in dichloromethane; only a 6.6% yield is obtained by the 60-min irradiation. The magnitudes of $G(\text{PhI})$ in the oxygen-containing solvents, such as methanol, THF, 1,2-dimethoxyethane, 1,4-dioxane, and acetone, suggest the occurrence of a chain reaction. (The symbol G represents the yield in molecules of a product for a 100-eV energy absorbed by the medium.)

The yield of Ph_2S from Ph_3SPF_6 varies much less with solvent than that of PhI from Ph_2IPF_6 . The $G(\text{Ph}_2\text{S})$ value is not beyond 3.0, suggesting that no chain reaction occurs for Ph_3SPF_6 . It is very small in dichloromethane.

The salts decompose through the one-electron reduction in the oxygen-containing solvents and acetonitrile. This has been revealed by the pulse radiolysis experiments. Pulse radiolysis of solutions of aromatic compounds in these solvents results in the formation of the solute radical anions via attachment of the solvated electrons or via charge transfer from the solvent anions, the latter of which is the case of acetone and acetonitrile. The effect of the added salts on the formation of the aromatic radical anion was investigated by using *trans*-stilbene ($5 \times 10^{-2} \text{ mol dm}^{-3}$) as the aromatic solute. The formation of the *trans*-stilbene radical anion was suppressed by the addition

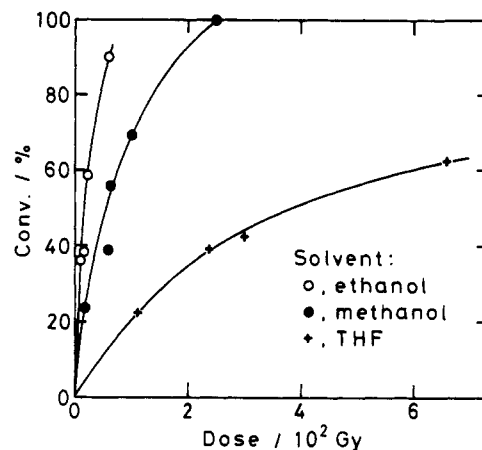
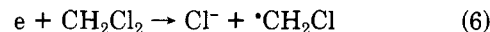


Figure 1. Yields of PhI in the radiolysis of Ph_2IPF_6 as a function of absorbed dose. The dose rates are (O, •) 1×10^2 and (+) $6 \times 10^2 \text{ Gy h}^{-1}$.

of $1 \times 10^{-2} \text{ mol dm}^{-3}$ salts. This suggests that the salts scavenge the solvated electron or the solvent radical anion to decompose through the one-electron reduction. The $G(\text{Ph}_2\text{S})$ values for these solvents may be close to the G values of the reducing species scavenged by Ph_3SPF_6 .

The decomposition of the salts is much less pronounced in dichloromethane than in the other solvents. Dichloromethane scavenges an electron to give a chloride anion, which is inert to the salts. The decomposition of the salts



occurring in dichloromethane is considered to proceed through the excited states similar to the case of the photolysis. The quantum yields of the formation of aryl iodides and diaryl sulfides in the photolysis of diaryliodonium and triarylsulfonium salts have previously been determined in acetonitrile.^{2,5,11} They are in the range of 0.17 to 0.34. There is no significant difference in the quantum yields between the diaryliodonium and triarylsulfonium salts. On the other hand, in the radiolysis of the solutions of Ph_2IPF_6 and Ph_3SPF_6 in dichloromethane, the $G(\text{PhI})$ value is appreciably large compared with the $G(\text{Ph}_2\text{S})$ value. This means an occurrence of additional reactions for Ph_2IPF_6 . No explanation for this observation can be offered at the present time.

The one-electron reduction of Ph_2IPF_6 in the oxygen-containing solvents is followed by a chain reaction. The decomposition rate of the salt was extremely high in ethanol as well as in methanol and in THF. The radiolysis of these solutions was carried out at lower dose rates, 1×10^2 and $6 \times 10^2 \text{ Gy h}^{-1}$, in order to determine the valid $G(\text{PhI})$ values. Figure 1 shows the yields of PhI plotted against absorbed dose. The $G(\text{PhI})$ values determined in the early stage of the radiolysis in ethanol, methanol, and THF are 2.8×10^3 , 1.8×10^3 , and 2.2×10^2 , respectively. The magnitudes of the $G(\text{PhI})$ values suggest that the kinetic chain lengths are of the order of 10^2 – 10^3 .

Further experiments for Ph_2IPF_6 were carried out in mixed solvents, and the results are presented in Table II. The contribution of alcoholic solvents to the chain reaction of the salt was investigated for methanol, ethanol, and 2-propanol. A comparison was made on the $G(\text{PhI})$ values for the mixed alcohol-acetonitrile solvents of a 1/1 volume ratio because of the low solubility of the salt in pure 2-propanol. Acetonitrile was chosen because in this solvent the salt decomposes through the one-electron reduction as well as in the alcohols but no chain reaction is initiated. As is shown in Table II, the $G(\text{PhI})$ values in the mixed solutions containing the alcohols increase in the order

Table II. Yields of PhI in the Radiolysis of Solutions of Ph₂IPF₆ in Mixed Solvents (1/1 Volume Ratio) at 0 °C^a

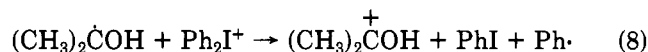
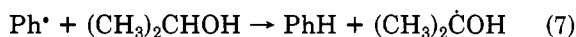
solvent	dose rate, Gy h ⁻¹	convn, %	G
2-propanol-acetonitrile	1 × 10 ²	32	2.4 × 10 ³
ethanol-acetonitrile	1 × 10 ²	11	7.7 × 10 ²
methanol-acetonitrile	1 × 10 ²	5.2	3.8 × 10 ²
1,2-dimethoxyethane-acetonitrile	5 × 10 ³	13	1.8 × 10
1,2-dimethoxyethane-dichloro- methane	5 × 10 ³	11	1.2 × 10

^aThe irradiation time and the salt concentration were 10 min and 1 × 10⁻² mol dm⁻³, respectively.

methanol < ethanol < 2-propanol. The oxidation potentials ($E_{1/2}$) of the α -hydroxyalkyl radicals derived from methanol, ethanol, and 2-propanol, reported in the literature, are -0.98, -1.18, and -1.30 V (vs SCE), respectively.³⁹ The lower oxidation potentials of the radicals result in the larger $G(\text{PhI})$ values. Furthermore, the $E_{1/2}$ values of the α -alkoxyalkyl radicals derived from THF and 1,4-dioxane have recently been reported to be -0.35 and -0.08 V (vs SCE), respectively.⁴⁰ As is shown in Table I, the $G(\text{PhI})$ values in the pure solvents decrease in the order methanol > THF > 1,4-dioxane. The $G(\text{PhI})$ values are also correlated to the oxidation potentials of the radicals. These results are evidence for the chain reaction involving the oxidation of the radicals derived from the solvents.

The radiolysis of the solutions of Ph₂IPF₆ was also carried out in acetonitrile and dichloromethane solvents mixed with 1,2-dimethoxyethane. The $G(\text{PhI})$ values for these solutions are large enough to conclude the occurrence of the chain reaction. It should be noted that the chain reaction is initiated in the solution containing dichloromethane, which inhibits the one-electron reduction of the salt.

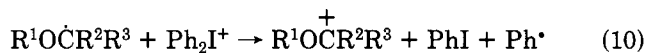
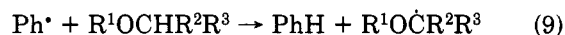
The following propagation steps have been proposed for the photolysis of diphenyliodonium salts in 2-propanol.^{12,21}



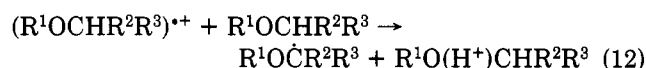
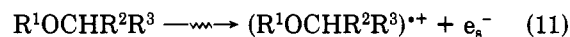
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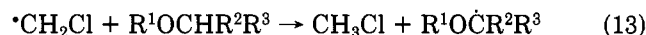
A similar chain reaction has also been reported to occur in the peroxide-initiated decomposition of diphenyliodonium salts in ethanol, 2-propanol,²¹ and mixed 1,4-dioxane-water.⁴¹ It is concluded that the chain reaction occurring in the radiolysis of the solutions of Ph₂IPF₆ in alcohols and ethers involves the oxidation of the α -hydroxyalkyl and α -alkoxyalkyl radicals derived from the solvents. The general expression of the propagation steps is as follows:



where R = H or alkyl. The radicals R¹O $\dot{\text{C}}$ R²R³ are radiolytically produced as well as reaction 9.



The $G(\text{PhI})$ value is very small in acetone compared with those in the other oxygen-containing solvents. This may be due to the fact that no radical oxidizable by the salt is produced directly from acetone. Small yields of byproduct radicals such as (CH₃)₂ $\dot{\text{C}}$ OH may contribute to the decomposition of the salt. In dichloromethane containing R¹OCHR²R³ the initiation of the chain reaction is due largely to the reaction of $\cdot\text{CH}_2\text{Cl}$, produced by reaction 6, as follows:



Contrary to the case of Ph₂IPF₆, the radicals produced from the oxygen-containing solvents are not oxidizable by Ph₃SPF₆. Therefore, no chain reaction occurs in the solutions of Ph₃SPF₆. This can be attributed to the lower reduction potential of Ph₃S⁺ compared with that of Ph₂I⁺; $E_{1/2}$ (V vs SCE) = -1.2 and -0.2 for Ph₃S⁺ and Ph₂I⁺, respectively.^{30,35}

Acknowledgment. We are grateful to the members of the Radiation Laboratory of this institute for help with the γ - and pulse-radiolysis experiments.

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