

Characterization of Iodonium Salts Differing in the Anion

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The properties and reactivity of a series of iodonium salts with different anions were compared. The nucleophilicity of the anions in such compounds can be characterized by their melting points and NMR spectra. When using Quinaldine Red as indicator and CH₃CN as solvent, the acid release rate of the iodonium salts correlated very well with their polymerization results in acid-sensitive epoxides.

Introduction

Diaryliodonium salts form the photoinitiator backbone of photocationic polymerization. First reported by Crivello and Lam and used for the polymerization of epoxides, diaryliodonium hexafluoroantimonates, and less so hexafluoroarsenates and hexafluorophosphates, are of particular value in commercial applications. As Crivello pointed out in early studies, only diaryl iodonium salts bearing nonnucleophilic counterions serve well as photoinitiators. The accepted reason is that nucleophilic gegenions such as chloride prematurely terminate the cationic chain reaction.

Several important problems have limited the commercial significance of the most photoreactive of the iodonium salts, the diaryliodonium hexafluoroantimonates. First, many salts containing low molecular weight symmetrical iodonium cations such as diphenyliodonium or ditolyliodonium are toxic and quite insoluble in monomer(s). Further there has been no general commercial supplier. The attention of the field has mainly focused on the onium cation. Crivello's group eventually synthesized a number of unsymmetrical salts such as *p*-octoxyphenylphenyliodonium hexafluoroantimonate (OPPI) and [(2-hydroxytetradecyloxy)phenyl]phenyliodonium hexafluoroantimonate (CD-1012), which were both less toxic and more soluble than their symmetrical counterparts. On the other hand, commercial cationic systems containing the more stable triarylsulfonium hexafluoroantimonates have been available since the mid-1980s in monomer/solvent mixtures from Union Carbide.

This changed dramatically recently with the introduction of non-nucleophilic organic anions such as tetrakis(pentafluorophenyl)borate by French workers³ and tet-

rakis(pentafluorophenyl)gallate by our group.⁴ 4-Methylphenyl-4-isopropylphenyliodonium tetrakis(pentafluorophenyl)borate is particularly soluble in silicone resins such as those used in release coatings. Its performance, matched or in some cases exceeded by diaryliodonium tetrakis(pentafluorophenyl)gallates, has become a benchmark in the field. Together, these two systems promise to greatly impact the use of iodonium salts in cationic photopolymerization.

Though mechanistic studies at various levels^{5,6} have clearly demonstrated how reaction intermediates form from diaryl iodonium salts, these have mainly focused on product and polymer analysis. We chose to develop a simple test in which one could measure the quantum yield of acid formation directly. In this paper, we use this test to measure the importance of anion on the photoacid genesis. We systematically compare the reactivities of a series of onium salts containing different anions and establish the relationship between structure, physical property, and reactivity.

Experimental Section

1. Materials. Acetonitrile (HPLC grade) and ethanol (HPLC grade) were purchased from Aldrich. Quinaldine Red (QR) was purchased from Acros Organics. 3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexanecarbonate (UVR 6110) was supplied by Union Carbide. (Octoxyphenyl)phenyl iodonium hexafluoroantimonate (HISbF₆) and tosylate (HIOTs) were gifts from GE Silicones. (Octoxyphenyl)phenyl iodonium chloride (HICl) was synthesized following a literature procedure.⁶ (3-Trimethylsilylpropoxyphenyl)phenyl iodonium chloride (ICl), hexafluoroantimonate (ISbF₆), and tetrakis(pentafluorophenyl)borate (IB) were synthesized as previously reported.⁷ Diphenyliodonium tetrakis(pentafluorophenyl)gallate (IVGa), (octoxyphenyl)phenyliodonium tetrakis(pentafluorophenyl)gallate (IIIGa),

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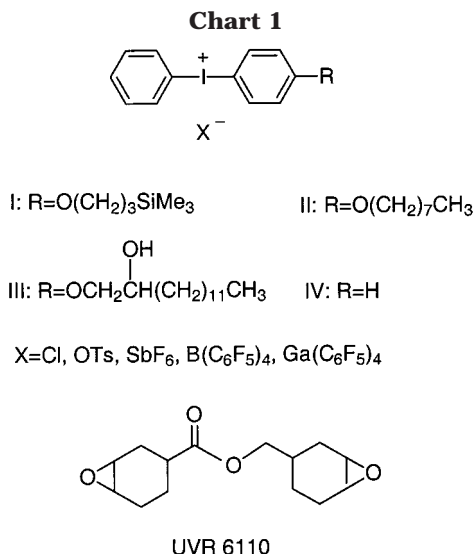
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(3-trimethylsilyloxyphenyl)phenyliodonium tetrakis(pentafluorophenyl)gallate (IGa), and [(2-hydroxytetradecyloxy)phenyl]phenyliodonium tetrakis(pentafluorophenyl)gallate (III Ga) were synthesized as reported.⁴ The structures of these iodonium salts and UVR 6110 are listed in Chart 1. (**Caution!** Preliminary toxicology studies of IIGa indicate potent dermal toxicity.)

Synthesis of (Octoxyphenyl)phenyliodonium Tetrakis(pentafluorophenyl)borate (IIB). IIOTS (0.58 g, 1 mmol) and KB(C₆F₅)₄ (0.78 g, 1 mmol) were mixed in CH₂Cl₂ and stirred for 4 h. After filtration, the solvent was evaporated to give a yellow sticky liquid with 94% yield. The crude product was purified by a short silica column. The compound was characterized by ¹H NMR and ¹⁹F NMR: ¹H NMR (CDCl₃, 200 Hz) δ 7.80–7.50 (m, 7H), 7.01 (d, 2H, *J* = 8.8 Hz), 3.98 (t, 2H, *J* = 6.6 Hz), 1.91–1.72 (m, 2H), 1.55–0.85 (m, 13H); ¹⁹F NMR (CDCl₃) δ -132.8 (sm, 2F), -162.8 (m, 1F), -166.7 (sm, 2F).

2. General Procedure for Measurement of Rate of Acid Release. Solutions (7 mM) of iodonium salts containing ~10 ppm Quinaldine Red in acetonitrile and ethanol were prepared. The initial absorbance of these solutions is 0.8 at 520 nm (in MeCN) or 530 nm (in EtOH). The solutions thus prepared were irradiated with different doses while the absorbance of QR at 520 nm (in MeCN) or 530 nm (in EtOH) was measured. The light source we used is a Fusion UV system F300 with H bulb. The lamp intensity is 300 W/in².

3. General Procedure of IR-Monitored Polymerization. Formulations containing 1 wt % initiator and 99 wt % UVR6110 were placed between two pieces of polyethylene spaced with a Teflon spacer (0.1 mm). The liquid film was irradiated in a Rayonet reactor equipped with 16 300 nm lamps. IR peaks at 790 and 1700 cm⁻¹ were monitored and integrated as a function of time. The peak at 1700 cm⁻¹ was used as the internal standard, and the conversion was calculated from eq 1. $\{(I_{790}/I_{1700})_0$ and $(I_{790}/I_{1700})_t$ are the area ratios of peaks at 790 and 1700 cm⁻¹ at the beginning and at time *t*, respectively}.

$$\text{conversion} = 1 - \frac{\left(\frac{I_{790}}{I_{1700}}\right)}{\left(\frac{I_{790}}{I_{1700}}\right)} \quad (1)$$

Results and Discussion

Physical Properties. Although the UV-vis absorption spectra of ICl, ISbF₆, and IB (Figure 1) show little difference, variations due to the structure of the anions are directly reflected in the melting points and NMR spectra. The former drop dramatically from ICl to IGa

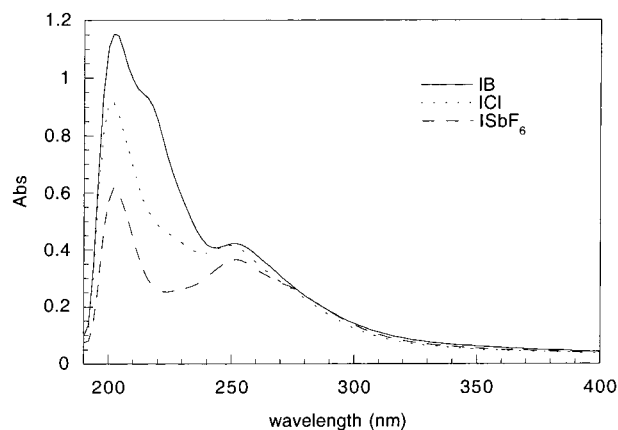


Figure 1. UV-vis absorption spectra of ICl, ISbF₆, and IB (2×10^{-5} M) in acetonitrile.

Table 1. Melting Points and Appearance of ICl, ISbF₆, IB, and IGa

	ICl	ISbF ₆	IB	IGa
appearance	powder	wax	sticky solid	viscous liquid
mp (°C)	169–170	54–56	48–51	NA

Figure 2. ¹³C NMR of ICl, ISbF₆, IB(C₆F₅)₄, and IGa(C₆F₅)₄ in CDCl₃.

(Table 1), while the appearance of these iodonium salts at room temperature changes from nicely shaped solids to amorphous viscous liquids. The factors responsible for the lowering of the melting point of the salts⁸ include the lessened symmetry of the cation, the addition of solvent-like functional groups that serve as solvent-soluble tails, the nonalignment of ion pairs, and the delocalization of the charge on the cation and anion. In our case, since the cations are identical, the only likely reason for lowered melting points is the delocalization of the various positive and negative charges. In other words, the ionic character decreases from chloride to tetrakis(pentafluorophenyl)gallate. Therefore, melting points are an indication of anion nucleophilicity.

The ¹³C NMR spectra of ICl, ISbF₆, IB, and IGa (Figure 2) show chemical shifts of C1 and C5 shifted upfield and those of the other carbons shifted downfield by a change in anion from Cl⁻ to Ga(C₆F₅)₄⁻. This suggests that the positive charge is less concentrated on

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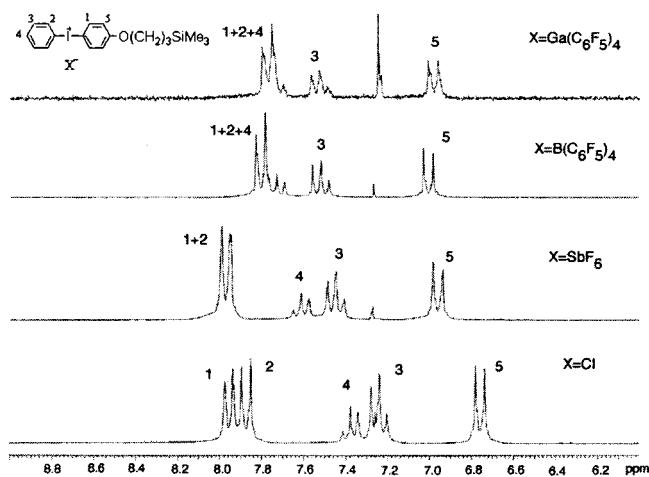
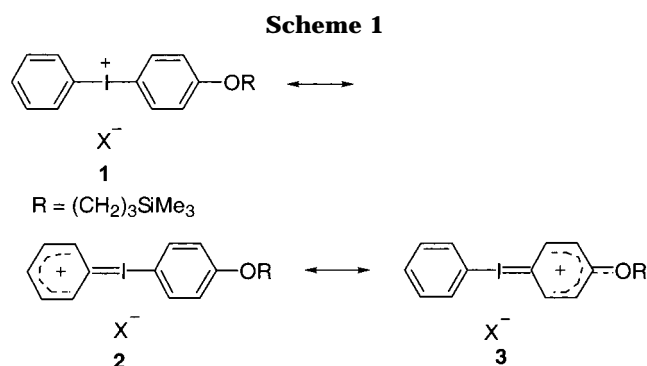


Figure 3. ^1H NMR of ICl , ISbF_6 , $\text{IB}(\text{C}_6\text{F}_5)_4$, and $\text{IGa}(\text{C}_6\text{F}_5)_4$ in CDCl_3 .



iodine in these salts, since it has been reported that once the oxidation state of the iodine is increased, the chemical shift of the ipso carbon moves downfield.⁹ Several resonance structures, the contributions to the hybrid of which vary as a function of the anion, can be drawn for the iodonium cation (Scheme 1). If the anion is Cl^- , the negative charge is localized on the chlorine atom. Accordingly, to stabilize the compound, the positive charge mostly localizes on the iodine and structure **1** dominates. However, when the anion is larger, the negative charge is more delocalized. Accordingly, the positive charge is also not just localized on the iodine. Instead, it delocalizes on the aromatic ring. In these cases, contributions from resonance structures **2** and **3** become important.

Consistent results were also obtained from the ^1H NMR spectra (Figure 3) with H1–H5 being assigned as labeled. When the anion is Cl^- , the positive charge mostly localizes on the iodine and the difference between H1 and H5 is large. When the negative charge of the anion is more delocalized, the positive charge of the iodonium salt disperses, decreasing the difference between H1 and H5. This delocalization also causes the chemical shifts of H1, H2, and H4 to be similar.

Thus, ^1H and ^{13}C NMR yield similar results. When the anion is changed from Cl^- to $\text{Ga}(\text{C}_6\text{F}_5)_4^-$, more positive charge disperses on the benzene ring instead of localizing on the iodine since from Cl^- to $\text{Ga}(\text{C}_6\text{F}_5)_4^-$ the electron density on the central atom of the anion decreases.

Acid Release. Since the initiating species is the proton in the case of cationic polymerizations initiated by onium

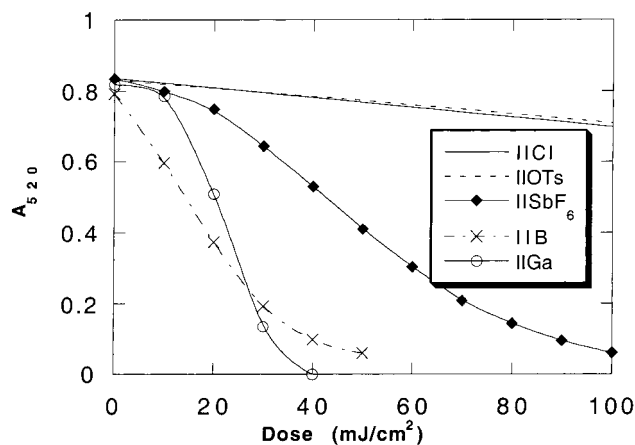
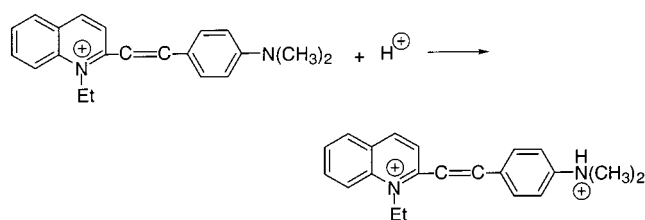


Figure 4. Acid release measurement of (octoxyphenyl)phenyl iodonium salts with different anions in acetonitrile.

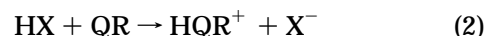
Scheme 2



salts, direct measurement of the formation of titratable acid offers an easy way to measure the photoreactivity of iodonium salts. Many methods have been developed to determine the acidity in nonaqueous systems,^{5a,10} though these are usually used for determining residual acidity. In our experiments, we developed a method to measure the rate of acid release upon photochemical exposure and used it to find the best solvent system to imitate an authentic photopolymerization condition.

Quinaldine Red (QR) is an indicator with an absorption band at 520 nm that is not observed for the protonated form (Scheme 2). When used in low concentrations, QR is essentially transparent below 350 nm where the iodonium salts absorb. A series of iodonium salts, **II**, differing in anion were irradiated in different solvents, and the bleaching of QR was observed quantitatively measuring the absorption spectra following different doses. In ethanol, a leveling solvent for acids, acid-release rates are almost identical. However, in acetonitrile, where there is limited protonation of the solvent, the anions can be differentiated and the acid release measurements correlated well with the photopolymerization results (Figure 4).

In the latter case, the bleaching rate of QR depends on the dissociation constant of the acid HX (eq 2). In this series, chloride is the most basic anion, so acid release is slowest in the presence of the chloride salt. Tetrakis-(pentafluorophenyl)borate and gallate are the least basic anions so the corresponding acids the strongest. The basicity of SbF_6^- lies between $\text{Ga}(\text{C}_6\text{F}_5)_4^-$ and Cl^- , which correlates well with the acid release rate as it was measured.



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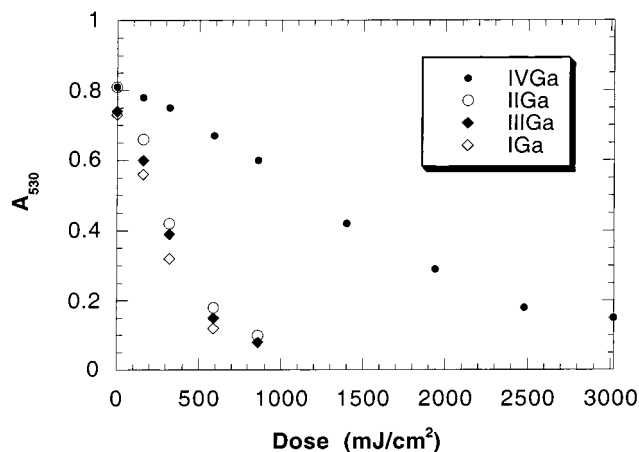


Figure 5. Acid release measurement of different iodonium tetrakis(pentafluorophenyl) gallates in ethanol.

A second series of iodonium salts differing in cation was also tested in both acetonitrile and ethanol. In this case, QR bleaching rates in acetonitrile did not distinguish the cations while those in ethanol did, suggesting that in acetonitrile there is no special interaction between the iodonium cation and the solvent. If the quantum yields and decomposition rates of the cations are similar, the bleaching rate of QR depends only on the acid strength of HX.

In the case of ethanol, the situation is different. It has been suggested that the oxygen atoms of properly substituted iodonium salts interact with the positive iodine,¹¹ and the oxygen of ethanol also likely interacts with the cation of the iodonium salt. Were structures of the iodonium salts to differ, such interactions would also differ resulting in varied decomposition rates of the iodonium salts in ethanol. From Figure 5 it seems that the symmetry of the cation plays an important role in this.

In conclusion, it is possible to measure the reactivity of iodonium salts as photopolymerization initiators by determining the rate of acid release in different solvents. By using CH₃CN one can distinguish the anions, while by using EtOH one can differentiate cations. The generality of this postulate was tested using other experimental methods.

IR-Monitored Photoinitiated Cationic Polymerization. Figure 6a shows the conversion of UVR6110, a cycloaliphatic epoxide,¹² initiated by a series iodonium salts **II** that differ only in the anions. The conversion to polymer and the rate of polymerization increase when the anions change from the nucleophilic Cl⁻ to the less nucleophilic Ga(C₆F₅)₄⁻. When using a series iodonium salts containing the same anion, Ga(C₆F₅)₄⁻, conversions were similar (Figure 6b). These results are consistent with those obtained in the acid release measurements in CH₃CN.

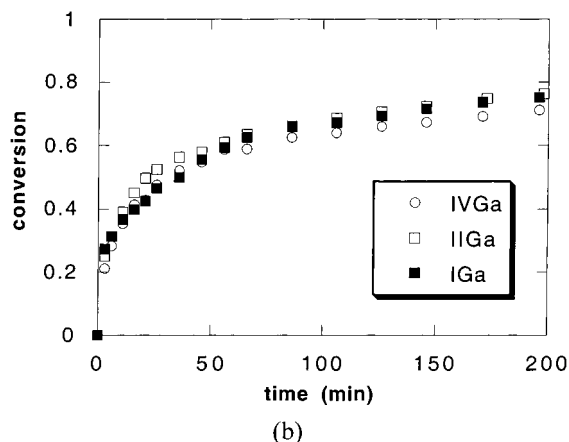
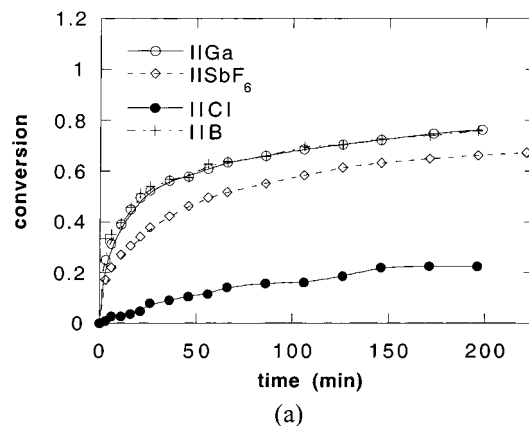


Figure 6. Conversion of polymerization of UVR6110 initiated by (a) (octoxyphenyl)phenyl iodonium salts with different anions and (b) different iodonium tetrakis(pentafluorophenyl)gallates.

Conclusion

A new method, acid release measurement, was developed to indicate the reactivities of iodonium salts as cationic photoinitiators. The properties and reactivities of a series of iodonium salts differing in the anion were compared, and it was found that the difference among these anions could be consistently reflected from their melting points, NMR spectra, acid release rates, and conversions after polymerization of acid sensitive epoxides. The decrease of the nucleophilicity from Cl⁻ to B(C₆F₅)₄⁻ and Ga(C₆F₅)₄⁻ can be characterized by melting points and NMR spectra, quantitatively measured from the bleaching rate of the indicator, QR, in certain solvents and from the conversion on the polymerization of similar monomers. We have also found that when the solubility of the iodonium salts in the same resin is similar, the effect of the cations on the reactivity will be much less than that of the anions.

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