Studies of Weakly Coordinating Anions Paired with Iodonium Cations[1]

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ABSTRACT: Several new iodonium salts containing weakly coordinating anions were synthesized and characterized. Upon UV irradiation, the rates of photoacid generation in acetonitrile and their preliminary activity in the photopolymerization of epoxy silicones were compared. Studies showed these salts to be excellent photoacid generators. The anions $[(C_6F_5)_3B-C_3H_3N_2-B(C_6F_5)_3]^-$, $B(C_6F_5)_4^-$, and $Ga(C_6F_5)_4^-$ were more active and the compounds made from them more soluble in most solvents. The $[(C_6F_5)_3B-C_6F_4-B(C_6F_5)_3]^{2-}$ anion was less active, and the compounds made from them were less soluble than compounds made from the three aforementioned anions. Compounds containing hexabromocarborane anion were quite similar to compounds containing SbF_6^- in both photoactivity and solubility.

Introduction

In recent years diaryl iodonium salts have been widely used as photoacid generators for catalyzing the cationic polymerization of many different monomers and oligomers. Upon irradiation with UV light, such salts undergo irreversible fragmentation with the generation of a Brφnsted acid which initiates cationic polymerization. This has been put to use in many different industries including for photolithography, as printing inks and release coatings, as well as in optical fibers and for holography.[2] In most common commercial salts, the counterion is the weakly nucleophilic inorganic anion SbF_6^-. Unfortunately, SbF_6^- salts exhibit poor solubility in nonpolar monomers or oligomers; they are often highly toxic and frequently somewhat hydroscopic. These drawbacks have recently been overcome with the discovery of salts of the tetrakis(pentafluorophenyl)borate anion by French scientists[3] and salts including the new anion tetrakis(pentafluorophenyl)gallate by us.[4] The strongly electron-withdrawing pentafluorophenyl groups contribute to the low oxidizability and general inertness of these anions. The fluorines also enhance the solubility of salts made from both anions when compared to their nonfluorinated analogues. In previous publications,[4−6] we reported that performance of salts made from the gallate exceeded those made from the borate in some cases. We believe that the weaker electronegative gallium contributes to the gallate anion being more weakly coordinating, and this makes compounds formed from it more photoactive in such instances.

Not only have salts of weakly coordinating anions been a subject of important research in the polymerization of epoxides and vinyl ethers, but they have also been intensely studied in olefin polymerization.[7] For example, $B(C_6F_5)_4^-$ has become one of the most extensively used anions over the past decade in this field. In homogeneous olefin polymerization, increasing the catalytic activity generally depends on the structure of anion in that the activity becomes higher as the anion in the catalyst becomes less nucleophilic. Accordingly, an important strategy is to reduce the nucleophilicity of anions by delocalizing their negative charge over two borate fragments. Examples of this approach would be monoanions with the formula $[(C_6F_5)_3B-LN-B(C_6F_5)_3]$, where the linking group (LN) is cyanide,[8] azide, dicyanamide, or imidazolide.[9] The most stable and effective LN is the imidazole, and the corresponding compound imidazole **1** is shown in Figure 1. In addition to distributing the negative charge of the anion over additional atoms, a second strategy would increase the efficiency of the perfluorophenyl group by using perfluorinated arenes as linking groups.[10−15] An example of such an anion can be seen in Figure 1 as compound dianion **2**.

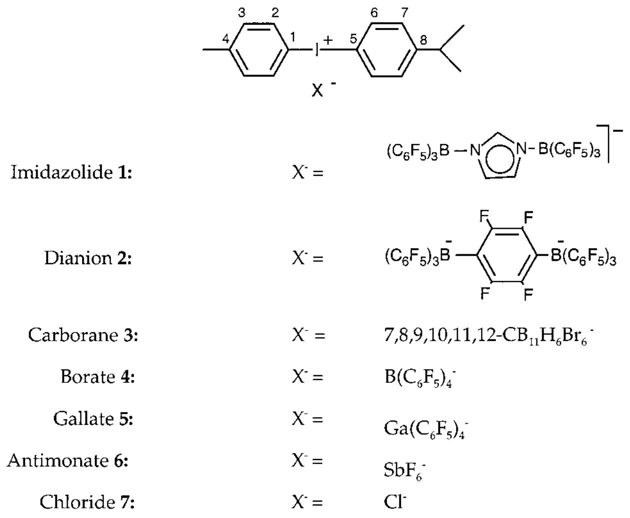

Figure 1. Structure of initiators.

Another new class of weakly coordinating anions has attracted intensive attention recently. These are based on the extremely stable boron cluster framework of monocarborane anions.[16,17] A series of halogenated derivatives of icosahedral $CB_{11}H_{12}^-$ have been reported. Typical examples include $CB_{11}H_6X_6^-$ (X = F, Cl, Br),[16−20] $CB_{11}(CF_3)_{12}^-$,[21] $CB_{11}F_{12}^-$,[20] and $CB_{11}F_{11}R^-$ (R = H, Me, Et, CF_3 etc.).[22,23] These weakly coordinating anions display extraordinary chemical, electrochemical, and

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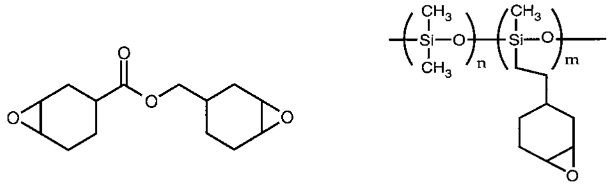


UVR 6110 **UV 9315**

Figure 2. Structure of resins.

thermal stability. The use of compounds containing some of these carborane counterions in olefin polymerization has been reported.[16,20]

With these characteristics in mind, we designed and synthesized several new iodonium salts containing the aforementioned weakly coordinating anions with borane skeletons. The main goal was to modify the borane architecture and compare the properties of each anion. Examples include diboranes **1** and **2** and the carborane **3**. Herein, we report the preparation and characterization of the (4-isopropylphenyl)-4′-methylphenyliodonium salts of these anions. The rate of photoacid generation of these salts is compared with those of $B(C_6F_5)_4^-$, $Ga(C_6F_5)_4^-$, SbF_6^-, and Cl^-, and an evaluation of the photoactivities in the polymerization of nonpolar epoxy silicon oligomor and polar cycloaliphatic epoxide monomer is reported. To our knowledge, no experiments pertaining to the use of these anions as photoacids in cationic epoxy polymerizations have been previously reported.

Experimental Section

Materials and Characterization Techniques. All manipulations were performed under an argon atmosphere using standard techniques. Reagents and solvents were purchased from Aldrich and used without further purification unless otherwise noted. Silver 7,8,9,10,11,12-hexabromocarborane was purchased from Strem Chemicals Inc., Newburyport, MA. Cycloaliphatic epoxide UVR 6110 (Figure 2) was purchased from Union Carbide Co. UV9315 (Figure 2) epoxy silicone oligomer [dimethyl-2-(7-oxabicyclo(4.1.0)hept-3-yl)ethyl, ((dimethyl-(2-(7-oxabicyclo(4.1.0)hept-3-yl)ethylsilyl)oxy) terminated] was obtained from General Electric Silicones. (4-Isopropylphenyl)-4′-methylphenyliodonium tetrakis(pentafluorophenyl)borate (**4**) (Rhodorsil 2074) was obtained from Rhodia. (4-Isopropylphenyl)-4′-methylphenyliodonium chloride (**7**), (4-isopropylphenyl)-4′-methylphenyliodonium hexafluoroantimonate (**6**), and (4-isopropylphenyl)-4′-methylphenyliodonium tetrakis(pentafluorophenyl)gallate (**5**) were prepared according to reported procedures.[4,24,25]

Caution: Preliminary toxicological testing on (octyloxyphenyl)phenyl iodonium tetrakis(pentafluorophenyl)gallate has shown the compound to be a potent dermal toxin. Therefore, similar structures, such as compound gallate **5**, should be handled with care, protecting the skin at all times.

^{1}H and ^{13}C NMR spectra were taken with a Varian Gemini 200 NMR spectrometer. ^{11}B and ^{19}F NMR were taken with a Unity Plus 400 NMR spectrometer. UV−vis spectra were obtained using a Varian Cary 50 scan spectrophotometer. Elemental analyses were performed by Altantic Microlab Inc. in Norcross, GA. Silica gel chromatography was performed using silica gel (40 μm, 32−63 μm) purchased from Scientific Adsorbents Inc. Melting points were uncorrected.

Preparation of $[(C_6F_5)_3B-C_3H_3N_2-B(C_6F_5)_3][HNEt_3]$. This synthesis was a slight modification of the procedure used by Lapointe and co-workers.[9] The mixture of triethylamine, tris(pentafluorophenyl)borane, and imidazole in toluene was refluxed for 5 h to give a white powder in quantitative yield. The crude product was used directly without further purification.

Preparation of $Li_2[(C_6F_5)_3B-C_6F_4-B(C_6F_5)_3]$. 1,4-Dibromotetrafluorobenzene (0.31 g, 1.0 mmol) in 20 mL of dry ether was cooled to −78 °C. BuLi (1.0 mL, 2.5 mmol) in hexane (2.5 M) was added dropwise at −78 °C. This solution was stirred for 30 min, and tris(pentafluorophenyl)borane (1.07 g, 2.0 mmol) in 30 mL of anhydrous ether was added dropwise. This mixture was stirred for 3 h and allowed to gradually warm to room temperature. The hazy solution was filtered, and the filtrate concentrated to give a light-yellow waxy oil (1.07 g). The crude product was used directly without further purification.

Imidazolide 1. $[(C_6F_5)_3B-C_3H_3N_2-B(C_6F_5)_3]$ $[HNEt_3]$ (0.41 g, 0.344 mmol) was dissolved in 15 mL of methylene chloride. To this solution, iodonium chloride (**7**) (0.14 g, 0.378 mmol) in 15 mL of methylene chloride was added at room temperature. The solution was stirred for 2 h in the dark. The precipitate was filtered, and the solvent removed to give a viscous oil (0.53 g). The crude product was chromatographed through a short plug of silica gel by elution with a mixture of CH_2Cl_2 and hexane (1:1) to give a white powder (0.45 g, 92% yield); mp 172−174 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 1.25 (d, 6H, J = 7.0 Hz, CH_3), 2.47 (s, 3H, CH_3), 3.00 (m, 1H, J = 7.4 Hz, CH), 6.76 (s, 2H, $C_3H_3N_2$), 7.49 (s, 1H, $C_3H_3N_2$), 7.38 (d, 2H, J = 8.4 Hz, C_6H_4), 7.42 (d, 2H, J = 8.8 Hz, C_6H_4), 7.80 (d, 2H, J = 8.6 Hz, C_6H_4), 7.81 (d, 2H, J = 8.6 Hz, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 23.5, 25.3, 36.2, 109.1, 109.2, 125.8, 130.3, 134.2, 136.5, 136.8, 148.5, 158.9. ^{11}B NMR ($CDCl_3$, $BF_3{\cdot}Et_2O$): δ −8.73 (s, 2B). ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −165.01 (s, 2F), −159.23 (s, 1F), −132.49 (s, 2F). Anal. Calcd for $C_{55}H_{21}B_2F_{30}IN_2$: C, 46.25; H, 1.48. Found: C, 46.45; H, 1.58.

Dianion Salt 2 was likewise synthesized from 2 equiv of iodonium chloride (**7**) and 1 equiv of $Li_2[(C_6F_5)_3B-C_6F_4-B(C_6F_5)_3]$ in 44% yield as a white powder; mp 120−122 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 1.26 (d, 6H, J = 7.0 Hz, CH_3), 2.48 (s, 3H, CH_3), 3.01 (m, 1H, J = 7.4 Hz, CH), 7.36 (d, 2H, J = 8.4 Hz, C_6H_4), 7.40 (d, 2H, J = 8.4 Hz, C_6H_4), 7.73 (d, 2H, J = 8.6 Hz, C_6H_4), 7.74 (d, 2H, J = 8.6 Hz, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 23.5, 25.4, 36.2, 109.1, 109.2, 125.8, 134.1, 136.8, 148.3, 158.7. ^{11}B NMR ($CDCl_3$, $BF_3{\cdot}Et_2O$): δ −16.78 (s, 2B). ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ −166.79 (s, 8F), −162.95 (s, 3F), −132.78 (s, 6F). Anal. Calcd for $C_{74}H_{36}B_2F_{34}I_2$: C, 48.14; H, 1.97. Found: C, 48.41; H, 2.15.

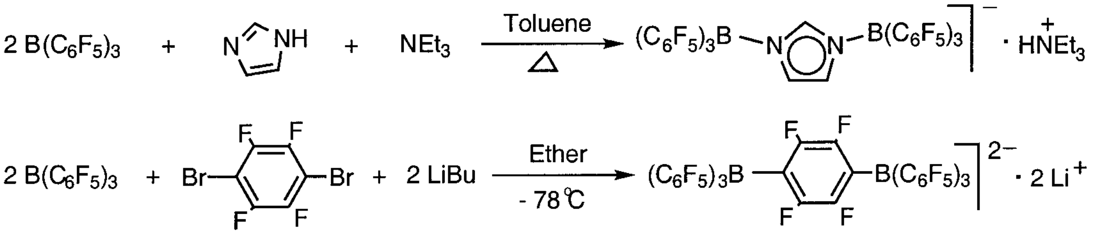
Carborane Salt 3 was likewise obtained from 1 equiv of the iodonium chloride (**7**) and silver 7,8,9,10,11,12-hexabromocarborane in 87% yield as a light-yellow powder; mp 180−182 °C. ^{1}H NMR ($CDCl_3$, TMS): δ 1.25 (d, 6H, J = 7.0 Hz, CH_3), 2.45 (s, 3H, CH_3), 2.98 (m, 1H, J = 7.4 Hz, CH), 7.36 (d, 2H, J = 7.8 Hz, C_6H_4), 7.40 (d, 2H, J = 6.4 Hz, C_6H_4), 7.91 (d, 2H, J = 8.8 Hz, C_6H_4), 7.92 (d, 2H, J = 8.8 Hz, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 23.6, 25.6, 36.2, 110.9, 111.0, 133.7, 136.2, 137.2, 147.3, 157.8, 162.7. ^{11}B NMR ($CDCl_3$, $BF_3{\cdot}Et_2O$): δ −20.15 (s, 5B), −9.88 (s, 5B), −1.54 (s, 1B). Anal. Calcd for $C_{17}H_{24}B_{11}Br_6I$: C, 21.41; H, 2.54. Found: C, 21.34; H, 2.67.

General Procedure for Measurement of Rate of Acid Release. Solutions of iodonium salts containing ~10 ppm of quinaldine red (QR) in acetonitrile were prepared at a concentration of 7.8×10^{-3} M. Since compound **2** is a dianion, it was prepared at 3.9×10^{-3} M. The initial absorbance of these solutions was ~1.6 at 520 nm. The solutions were irradiated at different doses under a UV lamp (System LC-06-T3 from American Ultraviolet Co.), while the absorbance of QR at 520 nm was measured. The conversion was calculated from the following eq 1, where A_0 was the absorbance at the beginning and A_n was the absorbance at dose n:

$$\text{conversion} = (1 - A_n/A_0) \times 100\% \qquad (1)$$

Photocure Degree in Cycloaliphatic Epoxide Monitored by FTIR. Solution of gallate **5** in monomer UVR 6110 at 1.00 wt % was prepared and used as a standard. The other iodonium salts were prepared at molar concentrations equal to gallate **5**, except for dianion **2** which was prepared at half the molar concentration due to its doubly charged anion. A drop of each solution in monomer UVR 6110 was placed

Scheme 1



between two pieces of polyethylene plates spaced with a Teflon spacer (0.015 mm). The liquid film was irradiated at different doses under a UV lamp (System LC-06-T3 from American Ultraviolet Co.). The IR peaks at 790 and 1730 cm^{-1} were followed by FTIR and integrated as a function of dose. The peak at 1730 cm^{-1} was selected as the internal standard, and the conversion was calculated from eq 2, where $(A_{790}/A_{1730})_0$ and $(A_{790}/A_{1730})_n$ are the area ratios of peaks at 790 and 1730 cm^{-1} at beginning and at dose n, respectively.

$$\text{conversion} = [1 - (A_{790}/A_{1730})_0/(A_{790}/A_{1730})_n] \times 100\% \quad (2)$$

Photocuring Test in Epoxy Silicone Resin. Borate **4** was dissolved at 0.25 wt % in an epoxy silicone resin (GE Silicones UV9315) and used as a standard. The other iodonium salts were prepared at molar concentrations equal to borate **4**, except for dianion **2**, which was prepared at half the molar concentration. Dianion **2**, carborane **3**, antimonate **6**, and chloride **7** were only partially soluble in the silicone resin and needed a cosolvent. Therefore, these compounds were first dissolved in diacetone alcohol (DAA, 4-hydroxy-4-methyl-3-pentanone) (3:1 solvent/initiator by weight) and then mixed with the silicone oligomer. A 0.5 mil film of these solutions was applied onto PK paper, and the sample was passed under a UV lamp (System LC-06-T3 from American Ultraviolet Co.) using a conveyor belt. The intensity of the UV lamp was 125 W/in^2. Whether or not the film was cured was determined by methods common to the current literature.[26] Firmly placing a thumb on the surface and dragging across the length of the coating was used to test the level of curing of the film. Any tackiness or smearing of the coating or transfer of the film to thumb was classified as a failure. The maximum speed of the conveyor belt that would provide curing without failure was recorded.

Discussion of Results

Preparation of Imidazolide 1, Dianion 2, and Carborane 3. The commercially available borate **4** contains a simple and unsymmetrical iodonium cation. This cation typically performs with high photoactivity and solubility in various epoxy resins. Therefore, other salts containing the same (4-isopropylphenyl)-4′-methylphenyliodonium were prepared for this study.

The reaction of 2 equiv of $B(C_6F_5)_3$ with 1 equiv of imidazole or triethylamine gave the corresponding ammonium salt as shown in Scheme 1. In similar fashion, 1 equiv of 1,4-dibromotetrafluorobenzene, allowed to react with 2 equiv of BuLi, gave the corresponding lithium dianion, which was quenched with 2 equiv of $B(C_6F_5)_3$ to give the desired lithium salt (Scheme 1). Iodonium chloride (**7**), when treated with the aforementioned ammonium and lithium salts, gave the desired imidazolide **1** and dianion **2** with satisfactory yield and high purity. Likewise, the silver hexabromocarborane was metathesized with iodonium salt (**7**) to give carborane **3**.

The purity of samples was very critical since even a slight trace of impurity might significantly decrease photoactivity, especially in epoxy polymerization. We found that chromatography was the most effective procedure to isolate the iodonium salts.

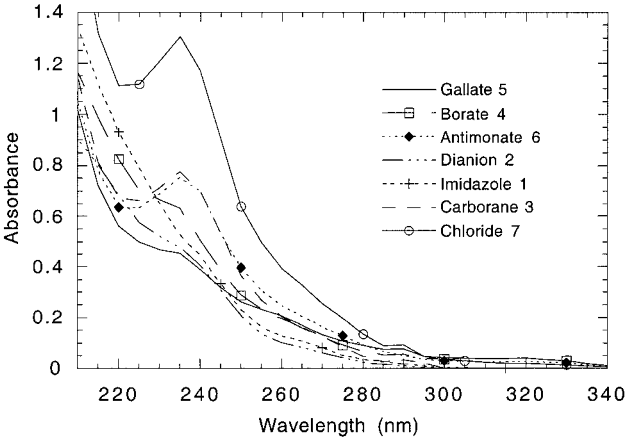


Figure 3. UV spectra of iodonium salts in ethanol (1.250 × 10^{-5} M) (dianion **2**: 6.125 × 10^{-6} M).

Comparison of UV Spectra. As expected from UV spectra, a hypsochromic effect was caused by the weakly coordinating anions. When compared to chloride **7**, the large size of the anion caused a greater delocalization of positive charge on the iodonium cation, and the $\pi \rightarrow \pi^*$ electronic transition energy of the iodonium salt was increased. Therefore, the absorption at the maximum wavelength (236 nm) was reduced roughly in the order of gallate **5** < dianion **2** < imidazolide **1** < borate **4** < antimonate **6** ≈ carborane **3** < chloride **7** (Figure 3). Unexpectedly, carborane **3** showed a similar UV absorption with antimonate **6**, even though the anion of carborane **3** was much larger than that of antimonate **6**. This foreshadowed the fact that both of them might display similar properties and activities.

Comparison of NMR Data. The anion determines the strength of the Brϕnsted acid deriving from the photolysis of iodonium salts and thus the propagation rate of the ensuing polymerization. We observe that the structure of the anion affected not only the UV absorption of the iodonium salt but also the NMR spectra. The ^{1}H and ^{13}C NMR chemical shifts in the spectra of compounds from imidazolide **1** to antimonate **6** are compared to those of chloride (**7**). The changes of the chemical shift ($\Delta\delta$) of carbons 1, 4, 5, and 8 as well as protons 2 and 6 (as labeled in Figure 1) are listed for each iodonium salt in Table 1 ($\Delta\delta = \delta_X - \delta_{Cl}$).

The ^{13}C NMR spectra of C1 and C5 of compounds **1**−**6** are shifted upfield when compared to chloride **7**, and those of C4 and C8 shifted downfield. The order of the compounds with regard to the magnitude of shift is borate **4** ≈ gallate **5** ≈ imidazolide **1** ≈ dianion **2** > antimonate **6** ≈ carborane **3**. Similar results are obtained from the ^{1}H NMR spectra for H2 and H6. Thus, it is reasonable to conclude that the larger chemical shift should correlate to a higher degree of oxidation on the

Scheme 2

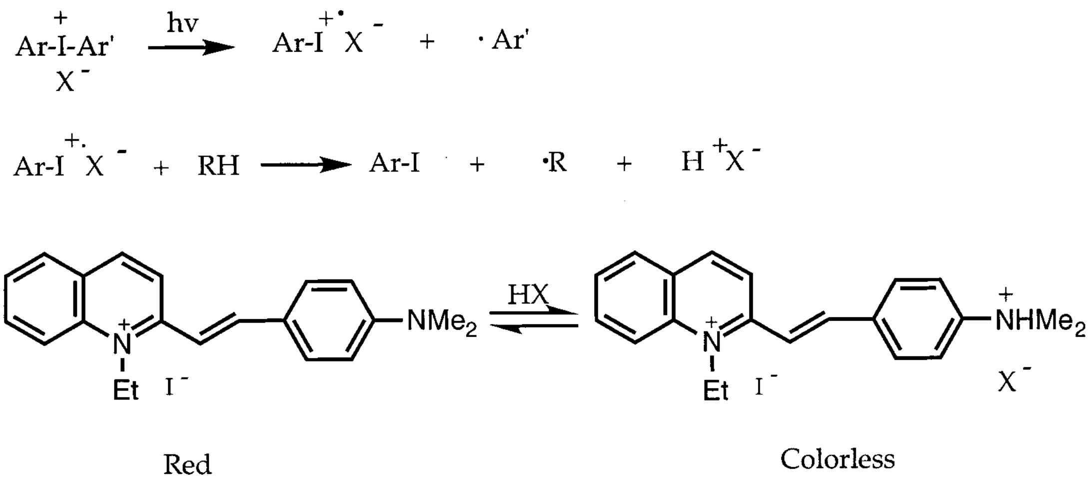


Table 1. Chemical Shift (Δδ) of Iodonium Salts and ^{13}C and ^1H NMR (Labeled in Figure 1)

	C1	C5	C4	C8	H2	H6
imidazolide **1**	−8.82	−8.89	4.97	4.84	−0.041	−0.040
dianion **2**	−8.73	−8.80	4.76	4.64	−0.087	−0.083
carborane **3**	−7.02	−7.14	3.83	3.71	0.059	0.066
borate **4**	−8.86	−8.92	4.88	4.75	−0.090	−0.086
gallate **5**	−8.84	−8.91	4.81	4.67	−0.102	−0.101
antimonate **6**	−7.37	−7.52	3.12	3.00	0.060	0.061

iodonium cation, a higher photosensitivity of the iodonium salt, greater distance between the cation and anion, a weaker coordination of the anion, and a stronger Bronsted acid formed upon irradiation. Consequently, anions of imidazolide **1**, dianion **2**, borate **4**, and gallate **5** should be similar to one another in the aforementioned properties. These four compounds should also be better than carborane **3** and antimonate **6**, whose properties should be similar to each other.

Comparison of the Rate of Acid Release. As mentioned before, iodonium salts undergo photolysis via an irreversible fragmentation process to generate the corresponding Brϕnsted acids. Among the several sensitive analytical methods developed to determine these acidic species,[6,27−29] the most effective in our hands is the system quinaldine red (QR) in acetonitrile. We observe that the photobleaching rate of QR correlates well with the basicity of the anions (Scheme 2).

From Figure 4, it should be noted that the order of photobleaching rate is as follows: gallate **5** > borate **4** > imidazolide **1** > carborane **3** > antimonate **6** > dianion **2** > chloride **7**. Iodonium salts imidazolide **1**, borate **4**, and gallate **5** exhibit higher photoactivity than carborane **3** and antimonate **6**. Of the three most active compounds, gallate **5** needs the shortest photoinduction time and imidazolide **1** the longest.

Surprisingly, dianion **2** does not follow our proposed thesis, and this compound is the second slowest save for the chloride **7**. A reasonable explanation is that the two negative charges in the anion $[(C_6F_5)_3B-C_6F_4-B(C_6F_5)_3]^{2-}$ are delocalized over seven aryl rings, and the density of negative charge of this anion is higher than that of $B(C_6F_5)_4^-$. Therefore, it is a stronger coordinating anion than $B(C_6F_5)_4^-$.

In the case of imidazolide **1**, only one negative charge is distributed over seven aryl groups of the anion $[(C_6F_5)_3B-C_3H_3N_2-B(C_6F_5)_3]^-$. This salt shows excellent activity, but the photoinduction time is much longer than that of $B(C_6F_5)_4^-$. This long induction period is probably due to the fact that the basic imidazole group in the anion neutralizes some of the generated acid. In addition, the curve slope of imidazole **1** is similar to those of gallate **5** and borate **4**. On the other hand, the slopes of compounds dianion **2** and carborane **3** are similar to that of antimonate **6**. These facts further suggest that imidazole **1** is a photoacid generator of high activity like gallate **5** and borate **4**, while dianion **2** and carborane **3** are similar to antimonate **6**. Compared to chloride **7**, all others show the characteristics of a superacid generator upon irradiation. These results are consistent with those obtained from the ^1H, ^{13}C NMR, and UV data analysis.

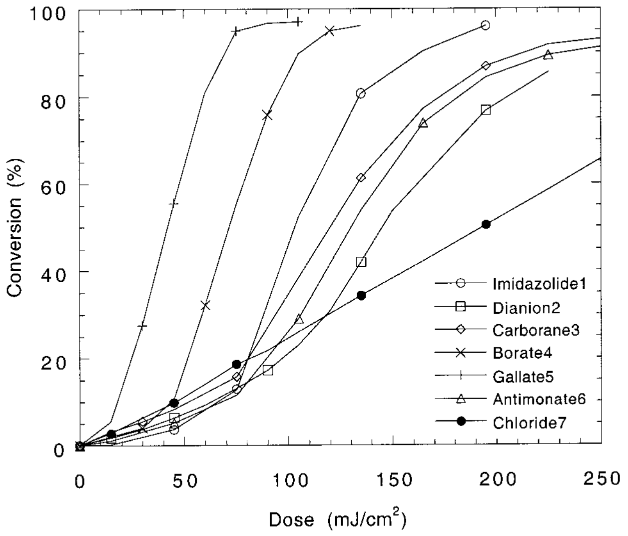


Figure 4. Rate of acid release of iodonium salts in acetonitrile.

Photopolymerization of Epoxy Resins. The performance of these iodonium salts in a polar resin UVR 6110 was investigated by FTIR (Figure 5). UVR 6110 was selected for this study because it dissolves all seven of the iodonium salts and because the epoxide band at 790 cm^{-1} is easily monitored by FTIR. A close examination showed that a slight difference in compounds **1**−**6** followed the order of gallate **5** > borate **4** > dianion **2** ≈ imidazolide **1** > carborane **3** ≈ antimonate **6** ≫ chloride **7**. All of compounds **1**−**6** exhibited high reactivity in this photopolymerization.

Photoacid generators with high solubility and activity in nonpolar media are of significant commercial interest

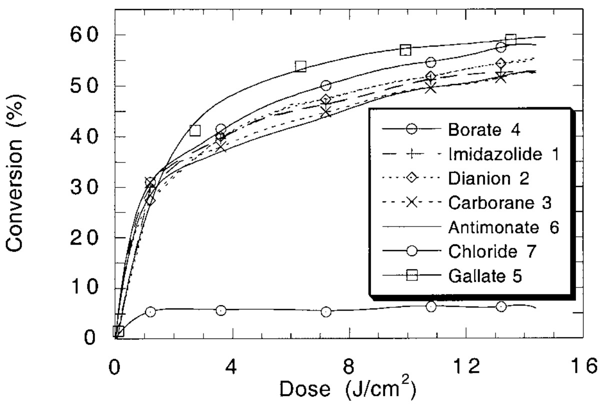


Figure 5. Conversion of UVR 6110 initiated by iodonium salts.

Table 2. Photoactivity of Iodonium Salts in UV9315[a]

compd	1	2	3	4	5	6	7
M_w	1429	1486/2	954	1016	1075	573	373
concn (wt %)	0.35	0.18	0.23	0.25	0.26	0.14	0.09
DAA (wt %)	−	0.75	0.75	−	−	0.75	0.75
solubility	+	+	−	+	+	−	−
activity (fpm)	28	22	13	28	28	3[b]	0

[a] +, solution was clear; −, solution was hazy; fpm = feet per minute. [b] The film was passed through UV three times at a belt speed of 10 fpm and estimated to be 3.

in industrial applications. For example, commercially available oligomer UV9315 is a silicone resin bearing a pendent epoxy-substituted cyclohexyl group. This oligomer is typically used in preparing release coatings for pressure-sensitive adhesives. Its successful application highly depends on the solubility and activity of the chosen photoacid generator. Unfortunately, the photopolymerization of this oligomer was difficult to monitor by FTIR because the IR band of the epoxy group overlapped with that of the siloxane functions.

Using another test method that determines the degree of cure by running samples on a conveyor belt under a UV lamp, the photoactivity of an equivalent concentration of the iodonium salts was evaluated in UV9315. The speed of the belt was increased until the samples fail to cure (see Experimental Section for details) (Table 2).

We observed that the order of solubility of the initiators in silicones was imidazolide **1** > gallate **5** > borate **4** > dianion **2** > carborane **3** > antimonate **6** > chloride **7**. Not surprisingly, the order of photoactivity was roughly similar to the order of solubility: gallate **5** ≈ borate **4** ≈ imidazolide **1** > dianion **2** > carborane **3** > antimonate **6** > chloride **7**. Because of their poor ability to mix with this silicone resin, dianion **2**, carborane **3**, antimonate **6**, and chloride **7** were first dissolved in diacetone alcohol (DAA), using a 3:1 ratio (by weight) of solvent to photoinitiator, and then added to the silicone oligomer. We noticed that such solution of dianion **2** was clear, but solutions of **3**, **6**, and **7** were hazy.

Imidazolide **1** was more soluble than either borate **4** or gallate **5**, but this did not correlate into better results as all three compounds exhibited the same high photoactivity. Even though dianion **2** could be completely dissolved in UV9315 after DAA was added, it still showed less photoactivity than imidazolide **1**, gallate **5**, and borate **4**, following the same trend observed in the acid release tests. Contrary to the acid release tests, dianion **2** outperformed carborane **3** and antimonate **6** in the polymerization of silicone oligomer. Additionally, carborane **3** and antimonate **6** displayed much lower activity than imidazolide **1**, dianion **2**, borate **4**, and gallate **5** in silicone oligomer. This is in agreement with our original hypothesis that compounds with similar NMR spectra exhibit similar photoactivities and rates of acid release.

Conclusions

A series of new, highly pure iodonium salts were synthesized by convenient preparative methods. Their NMR and UV spectra were compared. Iodonium salts containing the anions $[(C_6F_5)_3B{-}C_3H_3N_2{-}B(C_6F_5)_3]^-$, $B(C_6F_5)_4^-$, and $Ga(C_6F_5)_4^-$ were the most active and most soluble photoacid generators of the group that tested. $[(C_6F_5)_3B{-}C_6F_4{-}B(C_6F_5)_3]^{2-}$ was less active and less soluble than $B(C_6F_5)_4^-$ because of its higher density of negative charge on the anion. The hexabromocarborane anion was similar to SbF_6^- in both the activity and solubility of its iodonium salts. As a matter of fact, all were very good superacid generators and showed high activity in polar monomer. In addition, these salts were stable when neat samples were stored at room temperature in absence of light. As cationic photoinitiator of nonpolar epoxy silicone oligomer, imidazolide **1** was effective to catalyze the photopolymerization like borate **4** and gallate **5**, even though it exhibited longer photoinduction time in acetonitrile.

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