

# Carbocation Formation by Selected Hydrocarbons in Trimethylsulfonium Bromide–AlCl<sub>3</sub>/AlBr<sub>3</sub>–HBr Ambient Temperature Molten Salts

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**Abstract:** Using UV–visible and <sup>1</sup>H-NMR spectroscopy, the protonation of several hydrocarbons was studied in the Bronsted superacid molten salts, AlCl<sub>3</sub>–TMSuBr–HBr and AlBr<sub>3</sub>–TMSuBr–HBr (TMSu<sup>+</sup> = trimethylsulfonium, AlX<sub>3</sub>:TMSuBr mole ratio = 2) at ambient temperature. *m*-Xylene, mesitylene, pentamethylbenzene, hexamethylbenzene, and fluorene were completely protonated, and 1,1-diphenylethyl cation was formed in the AlCl<sub>3</sub>-based melt while the AlBr<sub>3</sub>-based melt allowed almost complete toluene protonation and *ca.* 30% benzene protonation (at *ca.* 0.02 M arene level) and diphenylmethyl cation generation. Since the NMR spectra of neutral and protonated arenes could be recorded for virtually identical solvents, it was possible to show that the positive charge distributions on the five sp<sup>2</sup> hybrid carbon atoms of pentamethylbenzenium ion obtained from the present <sup>1</sup>H- and earlier <sup>13</sup>C-NMR work were in agreement. The degradation of triphenylmethane in the two melts, with and without HBr, was shown to progress from the formation of triphenylmethyl cation, benzene, and diphenylmethane in less acid melts to the formation of triphenylmethyl cation, diphenylmethyl cation, benzene, and benzenium ion in AlBr<sub>3</sub>–TMSuBr–HBr.

## Introduction

The scope of carbocation studies in the AlX<sub>3</sub>–HX (X = Cl, Br) system<sup>2–6</sup> has been extended recently by the advent of ambient temperature haloaluminate melts. In particular, the electrochemistry of triphenylmethyl cation,<sup>7</sup> the preparation of anthracenium (and like) ions<sup>8</sup> and its investigation by <sup>2</sup>H-NMR,<sup>9</sup> and the UV–visible spectroscopic evaluation of arene protonation in melts of various Lewis acidities<sup>10</sup> have been carried out. The most studied ambient temperature melt is formed by mixing aluminum and 1-ethyl-3-methyl-1*H*-imidazolium (Im<sup>+</sup>) chlorides: it is liquid at ambient temperatures for AlCl<sub>3</sub> mole fractions of 0.33–0.67. Under a pressure of 1 atm of HCl, this system (with 67% AlCl<sub>3</sub>) was shown to be able to completely protonate fluorene but neither benzene nor toluene could be protonated.<sup>10</sup>

A stronger superacid would be expected to be formed from AlBr<sub>3</sub>, ImBr, and HBr, but the UV window would be narrower

than that of the chloride melt and furthermore the solvent <sup>1</sup>H- and <sup>13</sup>C-NMR signals for the Im<sup>+</sup>-based melts would likely interfere with those of added arenes and arenium ions. <sup>2</sup>H-NMR only provides a partial solution to the problems since the peaks are inherently broad and <sup>1</sup>H-<sup>2</sup>H exchange occurs at the 4,5-position of Im<sup>+</sup>.<sup>9</sup> We decided to capitalize on the discovery of Jones and Blomgren<sup>11</sup> that a 2:1 AlCl<sub>3</sub>:trimethylsulfonium chloride (TMSuCl) melt is liquid down to –50 °C by preparing and characterizing<sup>12</sup> the 2:1 AlCl<sub>3</sub>:TMSuBr and 2:1 AlBr<sub>3</sub>:TMSuBr melts from the commercially available TMSuBr. These melts are attractive for carbocation studies because (a) the UV window is wide since TMSu<sup>+</sup> is saturated unlike Im<sup>+</sup> and (b) the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra display only one sharp peak for the methyl nuclei, leaving wide NMR windows for solute resonances. This study describes the generation and recognition of several arenium ions, reports on the degradation of triphenylmethane in these solvents, comments on the positive charge distribution on the five sp<sup>2</sup> hybrid carbon atoms of pentamethylbenzenium ion, and discusses the acidity of several melts.

## Experimental Section

**Materials.** Trimethylsulfonium bromide (Eastman, 99%) was twice recrystallized from anhydrous ethyl alcohol (Aldrich) and dried under vacuum at about 40 °C for at least 3 days before use. The crystals obtained were colorless. Anhydrous hydrogen bromide obtained from Matheson was used as received. Anhydrous hydrogen chloride was prepared by the reaction of concentrated sulfuric and hydrochloric acids (Fisher ACS). To eliminate moisture from the reaction vessel, HCl was passed through a gas trap at –78 °C, two gas wash bottles filled with concentrated sulfuric acid, and a magnesium perchlorate column. Methylaluminum sesquichloride (MAC) (Aldrich) was used as received. The purification of anhydrous aluminum chloride and anhydrous

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aluminum bromide and the preparation of the 2:1  $\text{AlCl}_3$ :TMSuBr and 2:1  $\text{AlBr}_3$ :TMSuBr acidic melts have been described elsewhere.<sup>12</sup>

Benzene (Burdick & Jackson, distilled in glass), toluene (Fisher ACS), *m*-xylene (Eastman, 99.8%), mesitylene (Aldrich, Gold Label), durene (1,2,4,5-tetramethylbenzene) (Aldrich, 98%), pentamethylbenzene (Aldrich, 99%), hexamethylbenzene (Aldrich, 99+%), and fluorene (BDH) were used as received. Triphenylmethane (Lancaster, 98%) was twice sublimed in vacuo. Triphenylmethyl chloride (Aldrich, 98%), 1,1-diphenylethylene (Lancaster, 98%), benzhydryl chloride (chlorodiphenylmethane) (Lancaster, 97+%), and 2-bromo-2-methylpropane (*tert*-butyl bromide) (Eastman) were used as received.

**<sup>1</sup>H-NMR Spectroscopy.** <sup>1</sup>H-NMR spectra were obtained using a Bruker AC-200 NMR spectrometer equipped with a variable temperature unit. 3-(Trimethylsilyl)-1-propanesulfonic acid (sodium salt, Thompson-Packard) dissolved in dimethyl-*d*<sub>6</sub> sulfoxide was sealed into melting point capillaries and inserted into 5 mm NMR tubes as an external standard. NMR tubes were filled in the drybox, capped, and sealed with Parafilm before removal from the drybox. For NMR spectra obtained at temperatures lower than 10 °C, tetramethylsilane (TMS) dissolved in acetone-*d*<sub>6</sub> was used as an external standard; it was also presealed into melting point capillaries. The former standard resonates 0.49 ppm upfield from the latter one, and all of the chemical shifts presented in this paper are versus the former standard.

**UV-Visible Spectroscopy.** UV-visible spectra were measured with a Hewlett-Packard Model 8452A diode array spectrophotometer. Either 0.1 or 1 cm path length quartz cells were used. Spectra of protonated aromatic hydrocarbons were obtained with a quartz insert placed in a 0.1 cm quartz cell. Path lengths (50–200 nm) of the cells with inserts in place were calibrated using the 373 nm band of  $\text{K}_2\text{CrO}_4$  in 0.05 M aqueous KOH solutions ( $4842 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>13</sup> The 0.1 cm cell was first filled with an appropriate amount of melt, and then the insert was placed in the cell (making sure that there were no trapped bubbles). The cell was then sealed with Parafilm in the drybox. To make the sealing easier, inserts (8.5 × 47 mm) were made about 3 mm higher than the cell (10 × 44 mm).

**Protonation of Benzene and Methyl-Substituted Benzenes.** Solutions of aromatic hydrocarbons in 2:1 acidic melts were prepared by adding a weighed amount of hydrocarbon into a weighed volume (a few milliliters) of melt in a 10 mL serum bottle which was then capped with a septum. Molar concentrations were calculated from the densities of the melts.<sup>12</sup> In order to obtain NMR spectra with high signal-to-noise ratios, hydrocarbon concentrations were controlled between 0.2 and 0.6 M. Concentrations of hydrocarbons used for UV-visible measurements were much lower and, in order to minimize the error in weighing, solutions of *ca.* 0.02 M benzene and toluene in 2:1  $\text{AlBr}_3$ :TMSuBr were prepared by diluting 0.4 M solutions. After the bottle was removed from the drybox, it was first evacuated briefly to remove most of the nitrogen and with continuous shaking and HBr or HCl was introduced through a needle. Protonation reactions occurred very quickly as indicated by instant color changes. At about 1 atm of HCl or HBr, protonation reactions appeared complete in a few minutes for liquid hydrocarbons and in about 15 min for solid hydrocarbons as indicated by their dissolution. The resulting solutions were transferred back into the drybox and pipetted into NMR tubes or quartz cells for NMR or UV-visible measurements.

Most of the NMR spectra of neutral hydrocarbons were obtained by adding hydrocarbons to melts which had been treated with MAC to eliminate impurity protons. The reaction between MAC and impurity protons was slow when the proton concentration was low, and therefore, after adding MAC (*ca.* 0.02 M), the melts were shaken for a few minutes and then allowed to stand in the drybox for at least 2 hours before hydrocarbons were added.

**Preparation of Aryl- and Alkylarylmethyl Cations.** Triphenylmethyl cation,  $(\text{Ph})_3\text{C}^+$ , was prepared by adding a weighed amount of  $(\text{Ph})_3\text{CCl}$  into a weighed amount of 2:1  $\text{AlCl}_3$ :TMSuBr melt. 1,1-Diphenylethyl cation,  $(\text{Ph})_2\text{C}^+\text{CH}_3$ , was generated by the protonation of 1,1-diphenylethylene in 2:1  $\text{AlCl}_3$ :TMSuBr melt. The melt, in a serum bottle, was first saturated with HBr. While HBr was kept running through the bottle,  $(\text{Ph})_2\text{CH}=\text{CH}_2$  was added dropwise very slowly from

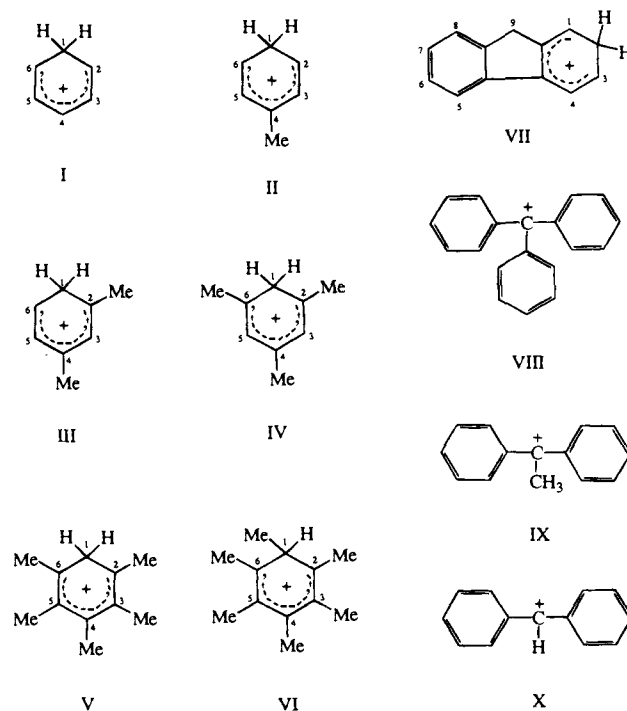


Figure 1. Carbocations prepared in this study.

a syringe. After each one-drop addition, the bottle was vigorously shaken until a homogeneous solution was formed. In this way, an approximately 0.2 M carbocation solution could be prepared easily. Diphenylmethyl cation (benzhydryl cation),  $(\text{Ph})_2\text{C}^+\text{H}$ , was prepared in a similar way by slowly adding benzhydryl chloride to 2:1  $\text{AlBr}_3$ :TMSuBr under an HBr atmosphere. The preparation of *tert*-butyl cation was attempted by slowly adding *tert*-butyl bromide to an  $\text{AlBr}_3$ :TMSuBr melt under an HBr atmosphere but seemed unsuccessful,<sup>14</sup> probably due to the rapid elimination reaction of *tert*-butyl cation to produce olefin at room temperature.

**General Practice.** All weighing and material transfers involving  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ , TMSuBr, and their mixtures were performed in a drybox under a nitrogen atmosphere. Traces of water and oxygen in the drybox were continuously removed by circulation through a purification train; a  $\text{P}_2\text{O}_5$  tray served as a visual check of moisture in the drybox. All materials and melts stored in the drybox were capped, sealed with Parafilm, and wrapped with aluminum foil. All the glassware was dried at  $>110$  °C overnight and then transferred quickly to the drybox.

## Results

The carbocations studied in this work are shown in Figure 1. Since the UV cutoffs ( $\lambda$  at absorbance = 1) of 2:1  $\text{AlBr}_3$ :TMSuBr and 2:1  $\text{AlCl}_3$ :TMSuBr are 228 and 210 nm, respectively,<sup>12</sup> it was possible to obtain the spectra of benzene, toluene, and their protonated ions in these melts. The data are tabulated in Tables 1 and 2 and illustrated for benzene and benzenium ion in Figure 2.

The <sup>1</sup>H-NMR spectra of the solvents are simple: the TMSu<sup>+</sup> methyl band, located at 1.52 ppm in the all-bromide melt and 1.90 ppm in the mixed halide melt, is flanked by four small bands, two spinning sidebands and two caused by <sup>1</sup>H-<sup>13</sup>C coupling with  $J = 146$  Hz. Table 3 lists the <sup>1</sup>H-NMR spectral data of benzene and selected methylbenzenes in the melts, in some cases with HBr and MAC added as indicated. Figure 3 compares the spectra of fluorene and fluorenium ion, and the chemical shift data appear in Table 4. The chemical shifts and coupling constants of the triphenylmethyl, 1,1-diphenylethyl, and diphenylmethyl cations are listed in Table 5. The spectra

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(14) In one case, two broad peaks at 2.83 and 2.40 ppm were found but the work was discontinued.

**Table 1.** UV Spectra of Benzene and Toluene in Melts at 23 °C and in Hexane

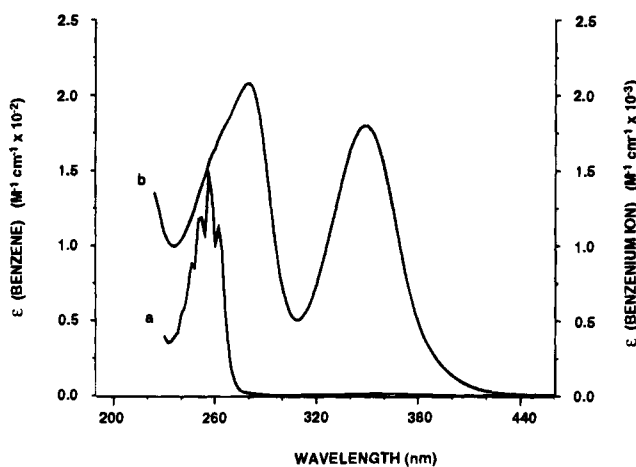
arene	$\lambda_{\max}$ , nm [ $\epsilon \times 10^{-2}$ , M <sup>-1</sup> cm <sup>-1</sup> ] <sup>a,b</sup>			
	AlBr <sub>3</sub> :TMSuBr	AlCl <sub>3</sub> :TMSuBr	AlCl <sub>3</sub> :ImCl <sup>c</sup>	hexane <sup>d,e</sup>
benzene	240 (s) [0.59]	240 (s) [0.54]		239 [0.54]
	246 [0.94]	246 [0.85]	242	243 [1.10]
	252 [1.2]	250 [1.2]	248 [1.65]	249 [1.90]
	256 [1.5]	256 [1.5]	254 [2.00]	254 [2.50]
	262 [1.2]	262 [1.1]	260 [1.40]	260 [1.70]
toluene	258 (s) [2.4]	256 (s) [2.1]		256 [1.90]
	264 [2.9]	264 [2.7]	261 [2.90]	262 [2.60]
	270 [2.4]	270 [2.1]	269 [2.45]	269 [2.40]

<sup>a</sup> s = shoulder. <sup>b</sup> 2:1 mole ratio for all melts. <sup>c</sup> Data from ref 10. <sup>d</sup> Data from *DMS UV Atlas of Organic Compounds*, Vol. I; Verlag Chemie: Weinheim, Germany, 1966, and Butterworths: London, 1966. <sup>e</sup> Some vibrational bands are not included.

**Table 2.** UV Spectra of Benzenium and Toluenium Ions in Melts at 23 °C

arene	$\lambda_{\max}$ , nm [ $\alpha\epsilon \times 10^{-2}$ , M <sup>-1</sup> cm <sup>-1</sup> ] <sup>a</sup>		
	AlBr <sub>3</sub> :TMSuBr	AlCl <sub>3</sub> :TMSuBr	AlCl <sub>3</sub> :ImCl <sup>b</sup>
benzene	280 [21]		325 [0.14]
	348 [18]	338 [0.23]	
toluene	272 [65]	264 [9.5]	
	346 [58]	332 [8.5]	328 [6.30]
		ca. 360 (s)	ca. 365 (s)

<sup>a</sup> s = shoulder. <sup>b</sup> Data from ref 10.

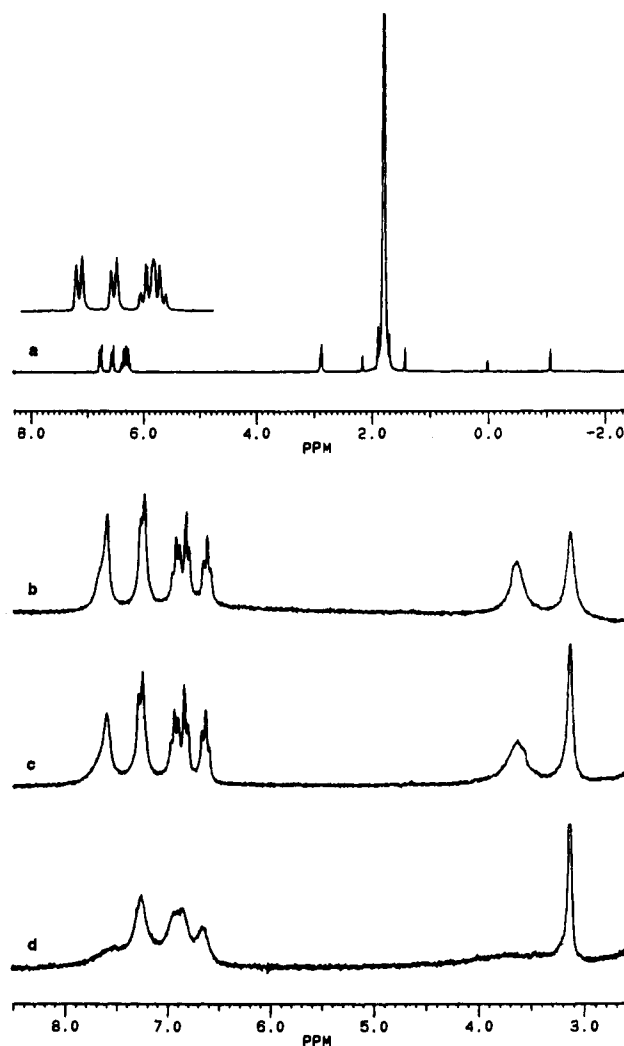
**Figure 2.** UV-vis spectra of benzene in (a) 2:1 AlBr<sub>3</sub>:TMSuBr with 0.02 M MAC and (b) 2:1 AlBr<sub>3</sub>:TMSuBr with HBr at 23 °C.

and the chemical species resulting from adding triphenylmethane to the two melts, with and without HBr added, are shown in Figure 4 and Table 6, and the four solutions are yellow in 2:1 AlCl<sub>3</sub>:TMSuBr, orange in 2:1 AlCl<sub>3</sub>:TMSuBr-HBr and in 2:1 AlBr<sub>3</sub>:TMSuBr, and deep red in 2:1 AlBr<sub>3</sub>:TMSuBr-HBr.

## Discussion

The UV spectra of benzene and toluene in the melts compare well with those in hexane except for the loss of some vibrational fine structure.<sup>15</sup> The UV-visible spectra obtained for benzenium and toluenium ions were stable for many hours and appear to be the first such spectra recorded for these species because no reliable spectra have been reported in the literature.<sup>16</sup> Using the estimate of  $(3-6) \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup> for the molar absorptivities of these ions by Smith et al.,<sup>10</sup> toluene and benzene (both

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**Figure 3.** <sup>1</sup>H-NMR spectra of (a) 0.3 M fluorene in 2:1 AlCl<sub>3</sub>:TMSuBr melt with 0.02 M MAC at 24 °C (upper trace: expanded ring proton signals) and 0.37 M fluorene in 2:1 AlCl<sub>3</sub>:TMSuBr melt with HBr (b) at -10 °C, (c) at 0 °C, and (d) at 24 °C.

at ca. 0.02 M) are protonated almost 100% and ca. 30%, respectively.

The arene solutions used for generating the NMR spectra of benzenium and toluenium ions were more concentrated (ca. 0.5 M) so that the degrees of protonation were somewhat less.<sup>10</sup> When HBr is added to the 2:1 AlBr<sub>3</sub>:TMSuBr melt at ambient temperature, the single NMR band for the ring protons of toluene (or benzene) broadens significantly and almost merges into the baseline, indicating that a rapid proton exchange process is occurring. The chemical shifts for the ring protons of toluene and benzene (Table 3) in the melt also change significantly (for benzene, from 6.05 to 5.36 ppm). Compared to the results obtained with very strong superacid systems such as SbF<sub>5</sub>-HF and SbF<sub>5</sub>-FSO<sub>3</sub>H at -80 °C,<sup>17a</sup> in which the single resonance for the ring protons of benzenium ion was found ca. 0.76 ppm downfield of that of neutral benzene in CDCl<sub>3</sub> at ambient temperature,<sup>17b</sup> the large upfield shifts observed for the ring protons of benzene and toluene in AlBr<sub>3</sub>-TMSuBr-HBr seem

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**Table 3.**  $^1\text{H}$  NMR Data of Arenium Ions and Their Corresponding Arenes in Melts

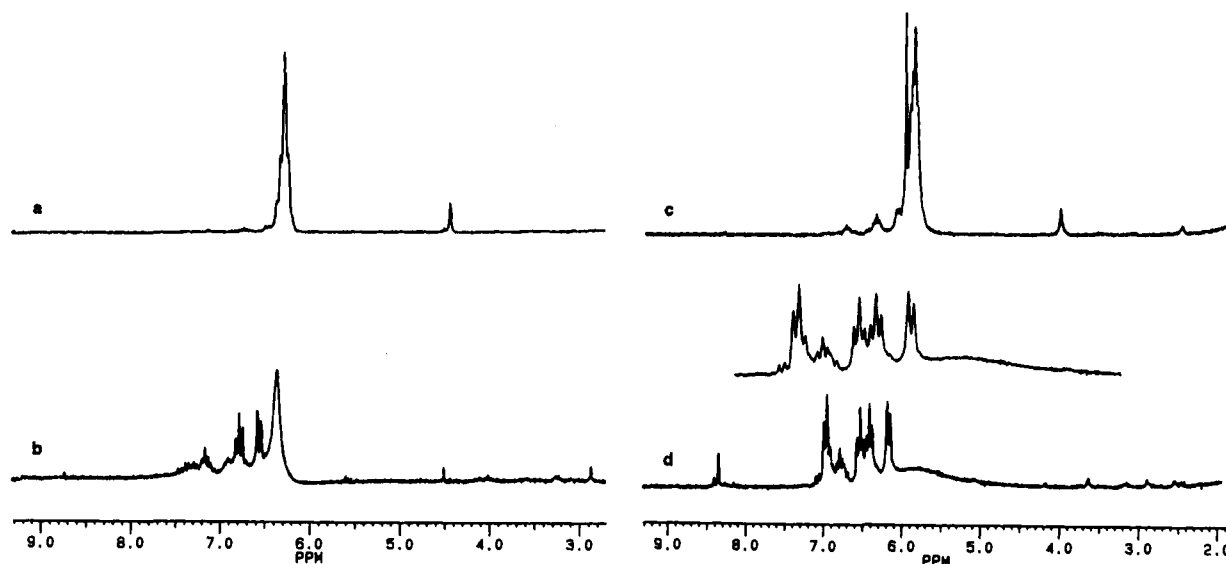
(arene) <sup>a</sup> arenium <sup>b</sup>	melt system	temp (°C)	chemical shift <sup>d</sup> of methyl (ring) protons				$\Delta\delta^e$ ppm
			C <sub>1</sub>	C <sub>2,6</sub>	C <sub>3,5</sub>	C <sub>4</sub>	
(I)	A	24	(6.05)	(6.05)	(6.05)	(6.05)	
I	B	24	(5.36)	(5.36)	(5.36)	(5.36)–	0.69
	B	5	(5.85)	(5.85)	(5.85)	(5.85)–	0.20
(II)	A	24	(5.86)	(5.86)	(5.86)	0.94	
II	B	24	(5.51)	(5.51)	(5.51)	1.39	+0.45
	B	5	(5.92)	(5.92)	(5.92)	1.46	+0.52
(II)	E	24	(6.24)	(6.24)	(6.24)	1.32	
II	D	24	(6.16)	(6.16)	(6.16)	1.51	+0.19
(III)	C	24	(6.06)	1.30 (6.21)	(6.06)	1.30	
III	D	24				1.84	+0.54
	D	0	(3.74)	1.84 (7.68)	(6.83)	1.84	+0.54
	D	–30	(3.74)	(7.68)	(6.83)		
(IV)	C	24	(5.86)	1.26	(5.86)	1.26	
IV	D	24	(3.49)	1.67	(6.53)	1.81	+0.55
(V)	C	24	(5.82)	1.17	1.10	1.14	
V	D	24	(3.57)	1.56	1.21	1.69 <sup>f</sup>	+0.55
VI	D	24	1.30 <sup>g</sup> (3.03)	1.30 <sup>g</sup>	1.30 <sup>g</sup>	1.30 <sup>g</sup>	

<sup>a</sup> MAC is added to melts to remove impurity protons; the excess generates a small band at –1.10 ppm. The TMSu<sup>+</sup> methyl proton signal is shifted 0.1 ppm upfield by addition of ca. 0.5 M solute. <sup>b</sup> See structures in Figure 1. <sup>c</sup> A, 2:1 AlBr<sub>3</sub>:TMSuBr–MAC; B, 2:1 AlBr<sub>3</sub>:TMSuBr–HBr; C, 2:1 AlCl<sub>3</sub>:TMSuBr–MAC; D, 2:1 AlCl<sub>3</sub>:TMSuBr–HBr; E, 2:1 AlCl<sub>3</sub>:TMSuBr. <sup>d</sup> In ppm. <sup>e</sup> Chemical shift difference of 4-methyl protons between neutral arene and protonated arene. <sup>f</sup> Triplet,  $J = 3.4$  Hz. <sup>g</sup> Doublet,  $J = 2.0$  Hz.

**Table 4.**  $^1\text{H}$  Chemical Shifts<sup>a</sup> of Fluorene (XI) and Fluorenum Ion (VII) in Melts

solute	C <sub>1</sub> <sup>b</sup>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>
(XI) <sup>c</sup>	6.57	6.28	6.37	6.78	6.78	6.37	6.28	6.57	2.88
(VII) <sup>d</sup>	7.62	3.66	7.67	7.28	7.28	6.64	6.94	6.83	3.15
$\Delta\delta^e$	+1.05		+1.30	+0.50	+0.50	+0.27	+0.66	+0.26	+0.27

<sup>a</sup> In ppm. <sup>b</sup> See structure VII in Figure 1. <sup>c</sup> In 2:1 AlCl<sub>3</sub>:TMSuBr–MAC at 24 °C. <sup>d</sup> In 2:1 AlCl<sub>3</sub>:TMSuBr–HBr at –10 °C. <sup>e</sup> Chemical shift difference between neutral and protonated fluorene.



**Figure 4.**  $^1\text{H}$ -NMR spectra of 0.25 M triphenylmethane in (a) 2:1 AlCl<sub>3</sub>:TMSuBr, (b) 2:1 AlCl<sub>3</sub>:TMSuBr–HBr, (c) 0.52 M triphenylmethane in 2:1 AlBr<sub>3</sub>:TMSuBr, and (d) 0.43 M triphenylmethane in 2:1 AlBr<sub>3</sub>:TMSuBr–HBr melt at 24 °C (upper trace: expanded ring proton signals).

unusual. This can probably be attributed to the proton exchange reaction of protonated benzene or toluene with HBr in the melt. However, the proton signal of HBr was not seen, even in melts saturated with HBr, but the corresponding signal has been observed at very high field using DCl in ImCl–AlCl<sub>3</sub> superacid melt;<sup>18</sup> the solubility of HBr in the bromide melts is probably less than 300 mM.

When the temperature is dropped to 5 °C, the lowest workable temperature for the AlBr<sub>3</sub>-based melt, the chemical shifts for the ring protons of benzene and toluene moved ca. 0.49 and

**Table 5.** Chemical Shifts and Coupling Constants of Carbocations VIII, IX, and X in Melts at 24 °C

cation	chemical shifts (ppm)					coupling constants (Hz)	
	CH <sub>3</sub>	H <sub>m</sub>	H <sub>o</sub>	H <sub>p</sub>	C <sup>+</sup> H	J <sub>p-m</sub>	J <sub>o-m</sub>
VIII <sup>a</sup>		6.78	6.58	7.15		7.33	7.72
IX <sup>b</sup>	2.54	6.69	6.85	7.11		7.27	7.81
X <sup>c</sup>		6.51	6.92	6.98	8.37	7.37	7.55

<sup>a</sup> In 2:1 AlCl<sub>3</sub>:TMSuBr. <sup>b</sup> In 2:1 AlCl<sub>3</sub>:TMSuBr–HBr. <sup>c</sup> In 2:1 AlBr<sub>3</sub>:TMSuBr–HBr.

0.41 ppm, respectively, downfield of those at 24 °C (Table 3) and the signals became narrower but still very broad. This indicates that the proton exchange reactions slow down by the

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**Table 6.** Species Resulting from Adding Triphenylmethane to Melts

2:1 melt	species identified <sup>a,b</sup>
AlCl <sub>3</sub> :TMSuBr	Ph <sub>3</sub> CH (6.26, 4.43), Ph <sub>3</sub> C <sup>+</sup> (trace)
AlBr <sub>3</sub> :TMSuBr	Ph <sub>3</sub> CH (5.86, 4.00), Ph <sub>3</sub> C <sup>+</sup> , PhH (5.97), Ph <sub>2</sub> CH <sub>2</sub> (5.86, 2.48)
AlCl <sub>3</sub> :TMSuBr-HBr	Ph <sub>3</sub> C <sup>+</sup> , PhH (ca. 6.30), Ph <sub>2</sub> CH <sub>2</sub> (ca. 6.30, 2.82), Ph <sub>3</sub> CH (ca. 6.30, 4.47), Ph <sub>2</sub> CH <sup>+</sup> (trace)
AlBr <sub>3</sub> :TMSuBr-HBr	Ph <sub>2</sub> CH <sup>+</sup> , Ph <sub>3</sub> C <sup>+</sup> , PhH, and PhH <sub>2</sub> <sup>+</sup> (5.8 region)

<sup>a</sup> Chemical shifts (ppm) in parentheses. <sup>b</sup> See Table 5 for the chemical shifts for Ph<sub>3</sub>C<sup>+</sup> and Ph<sub>2</sub>CH<sup>+</sup>.

decrease of temperature. At 5 °C a small downfield shift ( $\Delta\delta$  0.07 ppm) relative to that at 24 °C is also found for the methyl protons of toluene. Thus, a total of 0.52 ppm downfield shift relative to that of toluene at 24 °C is observed (Table 3). This means that at lower temperatures the protonation equilibrium favors arenium ion formation. The increased stability of arenium ion at lower temperatures will also slow down the intermolecular proton exchange between arenium ion and HBr in the melt.

Judging from the downfield shift of ca. 0.55 ppm (Table 3) for the 4-methyl protons upon protonation of *m*-xylene, mesitylene, and pentamethylbenzene, toluene ( $\Delta\delta$  0.52 ppm) in the 2:1 AlBr<sub>3</sub>:TMSuBr-HBr system should be almost completely protonated in the melt at 5 °C. In the 2:1 AlCl<sub>3</sub>:TMSuBr-HBr system, however, the downfield shift is much smaller ( $\Delta\delta$  0.19 ppm). Therefore, in this system, toluene is only partially protonated. Considering the small changes in band shape and chemical shift of benzene in 2:1 AlCl<sub>3</sub>:TMSuBr-HBr, it is virtually unprotonated but is partially protonated in the 2:1 AlBr<sub>3</sub>:TMSuBr-HBr system.

When HBr is added to the 2:1 AlCl<sub>3</sub>:TMSuBr melt containing *m*-xylene, the ring proton signals merge into the baseline because of the rapid intramolecular proton shift. The rate of the ring proton shift in the melt at 24 °C, however, is not very fast because it can be hindered effectively by a temperature decrease of only ca. 20 °C. The resolved NMR bands for ring protons at 0 °C can be sharpened by further decrease of temperature, but unfortunately, because of the increased viscosity of the melt at lower temperatures, the band for methyl protons of *m*-xylene merges into the much larger solvent (TMSu<sup>+</sup>) band. At temperatures lower than -30 °C, at which the melt becomes highly viscous, those bands for ring protons, as expected, broaden again. The relative areas of the three peaks centered at 7.68, 6.83, and 3.74 ppm are found, as expected, to be 1:2:2. Since no signals for unprotonated *m*-xylene could be observed in the spectra, the protonation of *m*-xylene by HBr in the melt should be complete under the experimental conditions. Although the values of the <sup>1</sup>H chemical shifts for *m*-xylenium ion listed in Table 3 are different from those obtained with other superacids in the literature because different standards have been used, the chemical shift differences between these bands are in good agreement with those observed in the solvents SbF<sub>5</sub>-HF and SbF<sub>5</sub>-FSO<sub>3</sub>H.<sup>19</sup>

<sup>1</sup>H-NMR spectral data of neutral and protonated mesitylene (IV) are listed in Table 3. The NMR spectrum of mesitylenium ion in AlCl<sub>3</sub>-TMSuBr-HBr is in good agreement with those obtained in other acid systems.<sup>19b,20</sup> No intramolecular proton

**Table 7.** Chemical Shift Changes ( $\Delta\delta_i$ )<sup>a</sup> and Charge Distributions ( $q_i$ )<sup>b</sup> from the Protonation of Benzene and Pentamethylbenzene

	benzene <sup>c</sup>		pentamethylbenzene		
	<sup>1</sup> H	<sup>13</sup> C	<sup>1</sup> H <sup>d</sup>	<sup>1</sup> H <sup>e</sup>	<sup>13</sup> C <sup>e</sup>
$\Delta\delta_{2,6}$	2.4	56.9	0.39	0.55	52.8
$\Delta\delta_4$	2.0	48.4	0.55	0.75	57.1
$\Delta\delta_{3,5}$	1.3	7.2	0.11	0.26	8.8
$q_{2,6}$	0.26 (0.32) <sup>f</sup>	0.32	0.25	0.23	0.29
$q_4$	0.21 (0.25)	0.27	0.35	0.32	0.32
$q_{3,5}$	0.14 (0.07)	0.04	0.07	0.11	0.05

<sup>a</sup> In ppm. <sup>b</sup> In electron charge units. <sup>c</sup>  $\Delta\delta$  values are calculated from the data in ref 17b. <sup>d</sup> This work, cf. Table 3. <sup>e</sup>  $\Delta\delta$  values are calculated from the data in ref 24. <sup>f</sup> Data in parentheses have been corrected for the electric field effect using a semiempirical relationship given in ref 21.

shift has been observed at ambient temperature, which confirms the conclusion that a high activation energy is needed for a ring proton to shift to a less basic carbon atom (with methyl substituent).<sup>21</sup> The agreement of the spectrum for hexamethylbenzenium ion (VI) in AlCl<sub>3</sub>-TMSuBr-HBr at ambient temperature is good with other spectra obtained under conditions of rapid intramolecular proton shift (e.g., above -20 °C in HF-BF<sub>3</sub> or HSO<sub>3</sub>F-SbF<sub>5</sub>).<sup>19b,22</sup> The chemical shifts of neutral and protonated pentamethylbenzene (V) are listed in Table 3. The spectrum of V agrees with those for other media.<sup>5b,19,20a</sup>

The cation V has been used as a model compound in evaluating the positive charge distribution on the dienyl system.<sup>21,23,24</sup> The strong linear correlation between charge and <sup>13</sup>C chemical shift in planar  $\pi$  ions has been widely verified.<sup>25</sup> By assuming that the positive charge is exclusively located on the five sp<sup>2</sup> hybrid carbon atoms and by neglecting any interactions between these partly charged carbons and other effects such as solvent, counterion, and substituent, one can calculate the positive charge fractions ( $q_i$ ) for the five ring carbon atoms according to the changes in chemical shifts ( $\Delta\delta_i$ ) of the ring carbons upon protonation (see Table 7). The obtained charge distribution on the five ring carbon atoms is in good agreement with those predicted by theoretical calculations.<sup>23,26</sup> The results of a similar calculation according to the <sup>1</sup>H  $\Delta\delta_i$  values for neutral and protonated benzene, however, are unsatisfactory (see Table 7). It has been pointed out by Kopytug and co-workers<sup>21</sup> that the electric field effect caused by other partly charged carbon atoms on the <sup>1</sup>H chemical shifts for the phenyl-ring protons is also important. After taking this into account, the obtained charge distribution (see Table 7, in parentheses) agrees much better with that calculated according to the <sup>13</sup>C chemical shift.

Previously, the  $\Delta\delta$  values for arenium ions were calculated relative to arenes in CS<sub>2</sub> or CDCl<sub>3</sub>, which introduces a solvent effect into  $\Delta\delta$  although it is not critical if the changes in chemical shift upon protonation are fairly large, e.g. <sup>13</sup>C chemical shifts of ring carbons (ca. 180 ppm/unit charge). In the case of methyl protons,<sup>21,24</sup> however, this effect is significant because the changes in chemical shift upon protonation are quite

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small (<2 ppm/unit charge). This problem can now be solved by the use of ambient temperature haloaluminate melts. Since pentamethylbenzenium ion solutions in  $\text{AlCl}_3\text{-TMSuBr-HBr}$  could be freed from excess HBr by 10 min of evacuation, the chemical shifts of both the arene and the ion were obtained in virtually the same solvent. The charge distribution on pentamethylbenzenium ion can be estimated according to methyl  $^1\text{H}$   $\Delta\delta_i$  values (Table 7) by assuming that the observed changes in  $^1\text{H}$  chemical shift of the methyl groups are exclusively caused by the excess charge at the ring carbon atom to which the methyl group is attached. For comparison, Table 7 shows the results calculated according to  $^1\text{H}$   $\Delta\delta_i$  data both measured in the  $\text{AlCl}_3\text{-TMSuBr}$  melt and obtained from ref 24, in which the chemical shifts of neutral pentamethylbenzene in organic solvent were used as reference points. It can be seen that the charge distribution estimated from the data obtained in the same solvent (the melt) agrees better with the result determined by  $^{13}\text{C}$ -NMR spectroscopy.

While the UV-visible spectrum of fluorenum ion was recorded in  $\text{AlCl}_3\text{-ImCl}$ ,<sup>10</sup> its NMR spectrum is unknown. Figure 3 indicates that the fluorene spectrum in  $\text{AlCl}_3\text{-TMSuBr}$  agrees well with that in  $\text{CCl}_4$ ;<sup>27</sup> the coupling constants between aromatic ring protons are 7.2 Hz. Addition of HBr gives a spectrum of very broad peaks at 24 °C with the 2- $\text{CH}_2$  proton signal almost merged into the baseline. Reducing the temperature to 0 °C inhibits the intramolecular proton shift and allows resolution into seven peaks of appropriate areas assigned as in Table 4. At -10 °C the broad 2- $\text{CH}_2$  signal at 3.66 ppm is narrowed somewhat. In agreement with the UV-visible work<sup>10</sup> and a basicity greater than that of *m*-xylene,<sup>28</sup> protonation appears complete.

Ambient temperature acidic haloaluminate melts quantitatively convert triphenylmethyl chloride into the triphenylmethyl cation (VIII). With the 200 MHz FT-NMR spectrometer the first-order  $^1\text{H}$ -NMR spectrum can be obtained (Table 5) and the ring proton signals readily assigned (labelling and computer modelling experiments<sup>29,30b</sup> are no longer needed). The stability of the ion is shown in the constancy of the spectrum over three months. 1,1-Diphenylethyl cation (IX) was prepared by protonating 1,1-diphenylethylene in 2:1  $\text{AlCl}_3\text{:TMSuBr/HBr}$  while diphenylmethyl cation (X) was obtained from chlorodiphenylmethane in 2:1  $\text{AlBr}_3\text{:TMSuBr/HBr}$ . The  $^1\text{H}$ -NMR spectra of both ions were unchanged after seven days. The spectra are better resolved than those previously obtained in other media,<sup>30</sup> allowing simple unequivocal assignments (Table 5).

A qualitative assessment of the products (Table 6) obtained by adding triphenylmethane to the melts is available from comparison of the composite  $^1\text{H}$ -NMR spectra (Figure 4) with those of individual species obtained in this work and that of  $\text{Ph}_3\text{CH}$  in  $\text{CDCl}_3$ .<sup>31</sup> Previous studies of the reaction of triphenylmethane with superacids showed that dealkylation to form diphenylmethyl cation and benzenium ions occurred in  $\text{SbF}_5\text{-HSO}_3\text{F}$  or  $\text{SbF}_5\text{-HF}$  (eq 1),<sup>32</sup> while in the weaker triflic acid,

the dealkylation was followed by hydride transfer to produce triphenylmethyl cation, diphenylmethane, and benzene (eq 2).<sup>33,34</sup>

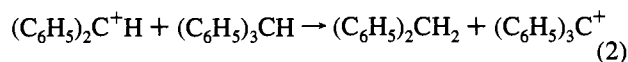
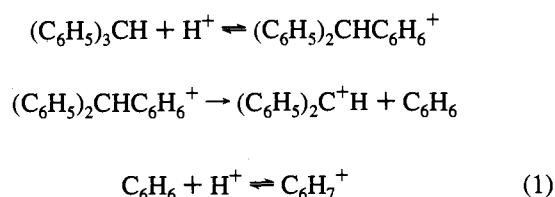
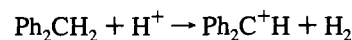


Figure 4a indicates that  $\text{AlCl}_3\text{-TMSuBr}$  leaves triphenylmethane alone while Figure 4b,c suggests that the increases in acidity on going to  $\text{AlBr}_3\text{-TMSuBr}$  and  $\text{AlCl}_3\text{-TMSuBr-HBr}$  lead to increasing dealkylation according to eq 2. In the  $\text{AlBr}_3\text{-TMSuBr-HBr}$  melt, however, the quantity of diphenylmethyl cation, as evidenced by peaks at 6.96, 6.5, and 8.37 ppm, is increased considerably; on the basis of peak intensities, the  $\text{Ph}_2\text{C}^+\text{H}:\text{Ph}_3\text{C}^+$  ratio is *ca.* 3:2. Although the rates and equilibria of protonation and dealkylation, and the rate of hydride transfer could explain the above ratio, the problem is the feeble signal for diphenylmethane (and/or protonated diphenylmethane) which should match the triphenylmethyl cation in concentration if there is no other reaction mechanism. One could write hydride abstraction (protonolysis)<sup>35</sup> steps such as



but there is no evidence of such a process in the stronger  $\text{SbF}_5$ -containing superacids. More definitive experiments on this system seem called for.

It is clear that the 2:1  $\text{AlCl}_3\text{:TMSuBr}$  and 2:1  $\text{AlBr}_3\text{:TMSuBr}$  melts with added HBr are Bronsted superacids. Since *m*-xylene ( $\text{p}K_{\text{B}} = 3.2$  in  $\text{HF}^{28}$ ) is completely protonated and toluene ( $\text{p}K_{\text{B}} = 6.3$  in  $\text{HF}^{28}$ ) is partly protonated in the mixed halide melt while toluene is almost completely protonated and benzene ( $\text{p}K_{\text{B}} = 9.4$  in  $\text{HF}^{28}$ ) is partly protonated in the all-bromide system, we see that the latter is decidedly more acidic with a Hammett acidity function 2–3 units more negative. Because toluene (or benzene) in both the  $\text{AlCl}_3\text{-TMSuBr-HBr}$  and the  $\text{AlCl}_3\text{-ImCl-HCl}$  systems is protonated to the same degree (within experimental error) (see Table 2), it is feasible to assume that these two melt systems have similar acidity. Actual  $H_0$  values can be assigned by reference to HF (pure but not 100%) where most authors have taken a value of -10 to -11.<sup>36</sup> If an  $H_0$  value of -10.7 was taken for HF, the  $H_0$  values for the systems of 2:1  $\text{AlCl}_3\text{:TMSuBr-HBr}$  (or 2:1  $\text{AlCl}_3\text{:ImCl-HCl}$ ) and 2:1  $\text{AlBr}_3\text{:TMSuBr-HBr}$  at 1 atm of HBr (or HCl) are *ca.* -14 and -16 to -17, respectively. Smith et al.,<sup>10</sup> however, used the value -15 for HF,<sup>37</sup> in that case, the  $H_0$  value for the  $\text{AlCl}_3$ -based melt would be *ca.* -18 instead of -14; we await further work to resolve this issue.

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