open shell electronic structure of these metallocenes and an appreciable ring π^* character to the empty or partially filled metal 3d orbitals. The core hole polarization in the C 1s excited states has a considerable effect on the spatial distributions of the virtual orbitals according to the EHT calculations.

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Registry No. $Fe(C_5H_5)_2$, 102-54-5; $Co(C_5H_5)_2$, 1277-43-6; $Ni(C_5H_5)_2$, 1271-28-9.

Quantitative Study of the Acidity of HCl in a Molten Chloroaluminate System ($AlCl_3$/1-Ethyl-3-methyl-1*H*-imidazolium Chloride) as a Function of HCl Pressure and Melt Composition (51.0–66.4 mol % $AlCl_3$)

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Abstract: The acidity of HCl in Lewis acid mixtures of $AlCl_3$ and 1-ethyl-3-methyl-1*H*-imidazolium chloride (EMIC) has been determined as a function of HCl pressure (P_{HCl}) and melt composition at ambient temperatures. The equilibrium constant (K'_B) for the protonation of arene bases (B) according to the reaction $HCl + B \rightleftarrows BH^+ + Cl^-$ was determined from the relation $\log K'_B = H' + \log([BH^+]/[B])$ with the protonation ratio measured spectrophotometrically and the acidity function, $H' = \log([Cl^-]/P_{HCl})$, evaluated by using the thermodynamic model of Dymek et al. to calculate $[Cl^-]$. Values of $\log K'_B$ were determined for chrysene, fluorene, 2-methylnaphthalene, and mesitylene over a range of HCl pressures and melt compositions, while estimates for benzene, toluene and naphthalene were obtained at a single pressure and composition (1 atm, 66.4 mol % $AlCl_3$). The correlation between $\log K'_B$ for these arenes in $HCl/AlCl_3$–EMIC and $\log K_B$ for the same arenes in HF/BF_3 suggests that $H' - H_0 \simeq 0.4$, where H_0 is the Hammett acidity function. According to this criterion H_0 for 0.01 atm HCl in 51 mol % $AlCl_3$ has a value of −12.6 (a superacid comparable to 100% H_2SO_4). At 1 atm HCl, a melt saturated with $AlCl_3$ at ambient temperatures (~67 mol % $AlCl_3$) is a much stronger superacid with a value of H_0 on the order of −18.

We recently showed[2] that when HCl is dissolved in a molten mixture of $AlCl_3$ and 1-ethyl-3-methyl-1*H*-imidazolium chloride (EMIC) containing 55.0 mol % $AlCl_3$ at ordinary temperatures and pressures it becomes a Brønsted superacid similar in strength to liquid HF ($H_0 = -15.1$[3]). The acidity of this mixture was determined by spectrophotometrically measuring the protonation of arene bases. 2-Methylnaphthalene proved to be a base of intermediate strength and was used for a quantitative study of the effect of HCl pressure on the Brønsted acidity. The results were consistent with the following simple chemical model. The protonation of an arene base (B) in an acidic $AlCl_3$–EMIC melt, i.e., one containing significantly more than 50 mol % $AlCl_3$, can be represented for thermodynamic purposes by eq 1. The

$$HCl + B \rightleftarrows BH^+ + Cl^- \qquad (1)$$

stoichiometric equilibrium constant for this reaction (K'_B) is given by eq 2, where $pK'_B = -\log K'_B$, Π is the protonation ratio

$$pK'_B = -\log \Pi + pCl + \log P_{HCl} \qquad (2)$$

($[BH^+]/[B]$), $pCl = -\log[Cl^-]$, and P_{HCl} is the pressure in atm of HCl in equilibrium with the melt. In these experiments pCl was fixed by the Cl^- exchange equilibrium given in eq 3, so that P_{HCl} was the only variable that affected the system acidity.

$$Cl^- + Al_2Cl_7^- \rightleftarrows 2AlCl_4^- \qquad (3)$$

Table I. Spectra of Arenium Ions in $AlCl_3$–EMIC (66.4 mol % $AlCl_3$) under ~1 atm HCl at 23 °C

starting arene	λ_{max} (nm) [$10^{-3}\epsilon$ (M^{-1} cm^{-1})]
fluorene	382 [33.3 ± $0.5^{a,b}$]
chrysene	268 [27.9], 296 [18.2], 340 [21.5], 525 [18.9 ± $0.3^{a,b}$]
2-methylnaphthalene	270 [3.6 ± 0.1^{c}], 400 [17.8 ± $0.4^{a,c}$]
mesitylene	262 [10.2], 360 [10.7^{a}]

[a] Band used to measure α. [b] Average of two independent measurements. [c] Average of three independent measurements.

We have now extended these studies to include melt composition as a variable, from 51.0 to 66.4 mol % $AlCl_3$. (The latter value is close to the solubility limit for $AlCl_3$ at ambient temperatures.[4]) We will show that the protonation of arenes of intermediate basicity responds to these changes in melt composition in the way described by eq 2 when pCl is calculated from previously measured thermodynamic properties of $AlCl_3$–EMIC melts.[5] Then we will examine the protonation of weakly basic arenes, including benzene. With these results we compare $HCl/AlCl_3$–EMIC with other strong Brønsted acids. In making this comparison it is instructive to treat eq 2 in terms of acidity function formalism. We define

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an acidity function (H') by eq 4 and note that according to eq

$$-H' = \log P_{\mathrm{HCl}}/[\mathrm{Cl}^-] = \mathrm{pCl} + \log P_{\mathrm{HCl}} \qquad (4)$$

2, this relation is equivalent to eq 5, which is analogous to the

$$-H' = \mathrm{p}K'_{\mathrm{B}} + \log \Pi \qquad (5)$$

standard definition of acidity functions including the Hammett acidity function (H_0; see, for example, ref 3). Note, however, that H', unlike other acidity functions, can be numerically evaluated without reference to indicator bases since $\log P_{\mathrm{HCl}}$ is a measured quantity and pCl is obtainable from existing data on the $AlCl_3$–EMIC system.[5] Also, the indicator bases used in the present study are different from those commonly used to measure H_0. The latter, as previously noted,[2] are probably complexed in acidic chloroaluminate melts in such a way as to be unsuitable for the present purposes.

Results and Discussion

The four arenes listed in Table I were used to measure the dependence of Π on P_{HCl} and melt composition. All were totally protonated under our most acidic conditions (1 atm HCl, 66.4 mol % $AlCl_3$) but only partially protonated under somewhat less acidic conditions. Spectra of the protonated arenes (arenium ions) are given in Table I. All were stable for at least several hours. Mesitylene, the strongest of these arene bases, was also totally protonated in melts with intermediate acidities, and the spectrum of its arenium ion measured under ~1 atm HCl in 55.5 mol % $AlCl_3$ as well as a previously measured spectrum in 55.0 mol % $AlCl_3$[2] were in excellent agreement with that reported in Table I. In a previous study[2] the ϵ value at 400 nm for protonated 2-methylnaphthalene was estimated from measurements in 55.0 mol % $AlCl_3$ (in which this arene is only partially protonated) by extrapolating data measured over a range of HCl pressures. This previous value was a little lower than that given in Table I.

The results of measurements of the effect of melt composition and HCl pressure at 23 °C on the degree of protonation are listed in Table II, where α is the fraction of the arene that was protonated so that $\Pi = \alpha/(1 - \alpha)$. Values of α were obtained with the formula $\alpha = A/(\epsilon b C_0)$, where A is the absorbance of an arenium ion band in a partially protonated mixture, ϵ is the molar absorptivity of that band taken from Table I, b is the cell path length in centimeters, and C_0 is the molar concentration of the arene prior to protonation. H' was computed from P_{HCl} and values of pCl derived from the thermodynamic model of Cl^- exchange equilibria in $AlCl_3$–EMIC developed by Dymek et al.[5b] The anionic fraction of Cl^- calculated from this model was converted to molar concentration by dividing by the molar volume of the melt computed from the density data of Fannin et al.[4]

The values of H' over which $\mathrm{p}K'_{\mathrm{B}}$ were measured varied from −16.62 to −13.53, a range of about 3.0, while $\mathrm{p}K'_{\mathrm{B}}$ for individual arenes were determined over H' ranges of about 1.6, except for the strongest base, mesitylene, which was restricted to an H' range of 0.7. The data for 2-methylnaphthalene in 55.0 mol % $AlCl_3$ are taken from the previous study[2] with $\mathrm{p}K'_{\mathrm{B}}$ recalculated by using ϵ from the present study (Table I). The previous value of $\mathrm{p}K'_{\mathrm{B}}$ was 14.6 while the values in Table II are slightly higher. Values of $\mathrm{p}K'_{\mathrm{B}}$ for each arene are constant to within about ±0.1. Thus the effects of melt composition and HCl pressure on the protonation of these arenes are represented reasonably well by eq 2.

Naphthalene in 66.4 mol % $AlCl_3$ under ~1 atm HCl was largely protonated with a band at 389 nm that had an $\alpha\epsilon$ value of 10.0×10^3 M^{-1} cm^{-1} [$\alpha\epsilon = A/(bC_0)$]. The corresponding band for fully protonated naphthalene in HF/BF_3[6] was at 390 nm with an ϵ of 10.9×10^3 M^{-1} cm^{-1}. Assuming that the latter value of ϵ also holds for the chloroaluminate melt, we estimate α to be about 0.9 and $\mathrm{p}K'_{\mathrm{B}}$ for naphthalene to be about 16.7. The naphthalenium ion was less stable in $HCl/AlCl_3$–EMIC than the arenium ions discussed above and was not studied further.

Table II. Protonation of Some Arenes by HCl in $AlCl_3$–EMIC at 23 °C

melt comp, mol % $AlCl_3$	P_{HCl}, atm	$-H'$	α	$\mathrm{p}K'_{\mathrm{B}}$
		Chrysene		
66.4	0.98	17.61	1.00	
63.8	0.98	16.55	0.65	16.3
63.8	0.20	15.86	0.28	16.3
63.8	0.12	15.64	0.19	16.3
63.8	0.06	15.34	0.12	16.2
63.1	0.98	16.38	0.58	16.2
57.2	0.98	15.38	0.17	16.1
55.0	0.98	15.07	0.11	16.0
		Fluorene		
66.4	0.94	17.61	1.00	
64.0	0.99	16.62	0.84	15.9
60.1	0.99	15.82	0.46	15.9
55.5	0.99	15.17	0.19	15.8
		2-Methylnaphthalene		
66.4	0.98	17.61	1.00	
60.1	0.98	15.81	0.90	14.9
55.0	0.98	15.07	0.67[a]	14.8
55.0	0.25	14.48	0.38[a]	14.7
55.0	0.18	14.34	0.31[a]	14.7
55.0	0.10	14.08	0.19[a]	14.7
55.0	0.08	13.98	0.17[a]	14.7
55.0	0.05	13.98	0.12[a]	14.7
54.1	0.98	14.93	0.61	14.7
51.0	0.98	14.15	0.22	14.7
		Mesitylene		
66.4	0.98	17.61	1.00	
55.0	0.98	15.07	1.00	
51.2	0.98	14.24	0.98	12.6
51.2	0.31	13.74	0.93	12.6
51.2	0.19	13.53	0.90	12.6
51.2	0.19	13.53	0.91	12.5

[a] Data from ref 2.

The spectra of benzene and toluene in 66.4 mol % $AlCl_3$ under ~1 atm HCl showed the bands of the unprotonated arenes and additional weak bands that we attribute to their arenium ions. The latter were at 325 nm with $\alpha\epsilon = 14$ M^{-1} cm^{-1} for benzene and 328 nm with $\alpha\epsilon = 630$ M^{-1} cm^{-1} and a shoulder at ~365 nm for toluene. For both arenes additional bands grew in at longer wavelengths indicative of decomposition reactions over periods of a few hours. Literature spectra with which to compare these results are limited. Luther and Pockels[7] reported the spectrum of the benzenium ion in benzene mixed with HCl and solid $AlCl_3$ and in benzene mixed with HBr and $AlBr_3$. The former system showed a band at 325 nm while the latter showed a band at 332 nm ($\epsilon = 3.8 \times 10^3$ M^{-1} cm^{-1}) and a very weak shoulder at ~420 nm. Toluene/$AlCl_3$/HCl mixtures[7] gave a band at 330 nm with flanking shoulders at ~327 and ~350 nm and a very weak band at ~500 nm, while toluene/$AlBr_3$/HBr[7] gave a band at ~350 nm with flanking shoulders at ~327 and ~375 nm. All of these spectra developed slowly because of slow mixing in these multiphase systems, and other bands appeared due to accompanying decomposition reactions. Bakoss et al.[8] studied benzene, toluene, and other arenes in CF_3SO_3H by ^1H NMR and UV spectroscopies and conductivity. Their spectra displayed more bands than those described above and underwent substantial time-dependent changes of unknown origin. These changes led them to comment that "CF_3SO_3H is a rather unsatisfactory solvent for spectrophotometric work, though it is clear that it fully protonates alkylated benzenes". The spectrum reported for the benzenium ion (in the format λ (nm) [$10^{-3}\epsilon$ (M^{-1} cm^{-1})]) was 325 [2.8] and 430 [2.8] and for the toluenium ion 335 [5.7], 454 [1.75], 522 [1.2], and 578 [1.0]. Although toluene could be recovered almost quantitatively from CF_3SO_3H after 24 h, it is tempting to suspect

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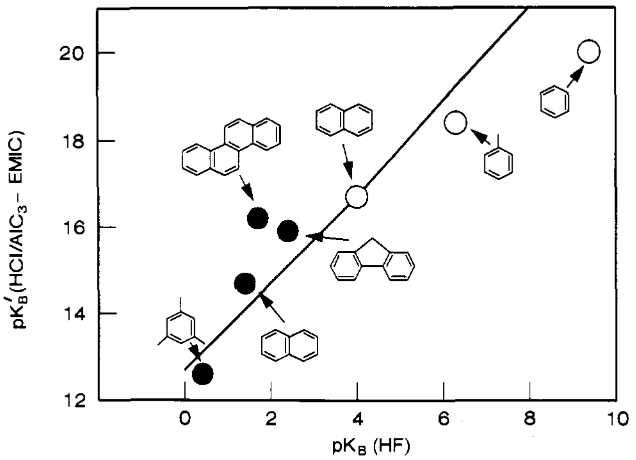

Figure 1. Correlation between the basicity constants of arenes in HCl/AlCl$_3$–EMIC (K'_B) reported here and those for the same arenes in HF/BF$_3$ (K_B) reported by Makor et al.[9] (○) K'_B estimated (see text); (●) K'_B based on data in Table II.

that some of these bands, particularly those at longer wavelengths, may have been due to intensely absorbing decomposition products.

Although we have not measured the molar absorptivities of the benzenium and toluenium ions in HCl/AlCl$_3$–EMIC, ϵ values for similar bands in other media are on the order of 3×10^3–6×10^3 M^{-1} cm^{-1}. If we assume these values for the 66.4 mol % AlCl$_3$ melt, we obtain for benzene α values of about 0.002–0.005 and a pK'_B value of 20.0 ± 0.2, while for toluene, α is about 0.1–0.2 and pK'_B equals 18.4 ± 0.2.

Figure 1 shows the correlation between pK'_B for the indicator arenes in HCl/AlCl$_3$–EMIC and the corresponding quantity (pK_B) for these same arenes in HF/BF$_3$ as reported by Makor et al.[9] Except for chrysene the order of basicity is the same for both media and the points follow a smooth trend. Why chrysene should be an exception is not clear. It is also interesting to note that except for chrysene and benzene the points lie within less than 1 pK unit of the straight line drawn in Figure 1. This line has unit slope and an intercept on the log K'_B axis of 12.7, which equals the average of the differences pK'_B – pK_B. Thus for each arene pK'_B – pK_B is approximately constant, so that the relative basicities of these arenes are similar in both media.[10]

As noted previously,[2] 2-methylnaphthalene is protonated to a similar extent in HF ($H_0 = -15.1$)[3] and in HCl/AlCl$_3$–EMIC with $H' = -14.7$. If we assume that, at least to a rough approximation, H_0 and H' maintain the same relative values, that is, $H' - H_0 = 0.4$ for melts containing 51 mol % or more AlCl$_3$, then the following estimates are obtainable. In melts containing 51 mol % AlCl$_3$, HCl at 0.01 atm has an H_0 value of approximately –12.6, a value comparable to that of 100% H$_2$SO$_4$ ($H_0 = -12.1$)[11] while at the solubility limit for AlCl$_3$ (~67 mol %),[4] H_0 is approximately –18 for 1 atm HCl. Furthermore, if the solid phase in equilibrium with the latter melt is AlCl$_3$, rather than some unidentified chloroaluminate salt, then H_0 is also –18 for the conjugate pair HCl (1 atm)/AlCl$_3$(s).

Experimental Section

Experimental procedures including the preparation and purification of compounds, except benzene and toluene, have been described.[2] Benzene and toluene (Aldrich Gold Label) were degassed by four freeze–pump–thaw cycles, dried over molecular sieves, and stored under argon.

Spectra of unprotonated benzene and toluene in 66.4 mol % AlCl$_3$ under argon were very similar to those in organic solvents, viz., λ (nm) [$10^{-3}\epsilon$ (M^{-1} cm^{-1})]: benzene in 66.4 mol % AlCl$_3$, 242, 248 [165], 254 [200], 260 [140]; benzene in cyclohexane,[12] 243 [99.3], 248.5 [169], 254 [212], 260.5 [149]; toluene in 66.4 mol % AlCl$_3$, 261 [290], 269 [245]; toluene in methanol,[12] 261 [238], 264 [167], 268 [222]. Spectra of the other six indicator arenes under argon in AlCl$_3$–EMIC melts of various compositions were the same as those previously reported for solutions in 55.0 mol % AlCl$_3$.[2] All were stable for at least several hours.

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Registry No. EMIC, 65039-09-0; HCl, 7647-01-0; AlCl$_3$, 7446-70-0; chrysene, 218-01-9; fluorene, 86-73-7; 2-methylnaphthalene, 91-57-6; mesitylene, 108-67-8; benzene, 71-43-2; toluene, 108-88-3; naphthalene, 91-20-3.

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