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OXIDATION OF ARENES BY MOLTEN GALLIUM(III) CHLORIDE

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Abstract: Molten, anhydrous Ga_2Cl_6 at 100-130°C readily oxidizes pyrene, anthracene and naphthacene with the concomitant reduction of Ga(III) to Ga(I). Dilute solutions of these arenes (ArH) are oxidized to their radical cations ($ArH^{+\bullet}$), which decay very slowly in Ga_2Cl_6, while more concentrated solutions are oxidized to stable arenium ions (ArH_2^+) with hydrogen derived from aryl-aryl coupling reactions.

There is a growing awareness of the importance of single electron transfer processes in organic reactions.[1] In this context we now report for the first time that gallium(III) chloride (Ga_2Cl_6)[2], which is well-established as a strong Lewis acid catalyst,[3] is also a moderately strong oxidizing agent capable of inducing stoichiometric oxidation reactions for pyrene (**1**), anthracene (**2**) and naphthacene (**3**), but not naphthalene (**4**), with the concomitant reduction of Ga(III) to Ga(I). We investigated these reactions in molten, high-purity Ga_2Cl_6 under inert atmospheres[4] at 100-130°C by *in situ* ^1H and ^{71}Ga NMR, ESR, and by product analysis following melt hydrolysis.

Dilute solutions (*ca.* 0.06 mol %) of **1**, **2** and **3** in molten Ga_2Cl_6 at 100°C underwent spontaneous oxidation to form very persistent radical cations, which were identified at 100°C from their strong ESR spectra with well-resolved hyperfine structure.[5] At moderate concentrations (*ca.* 2 mol %) a more complex oxidation reaction occurred in which 60-70% of the starting arene (ArH) was protonated to form stable arenium ions (ArH_2^+) and the remainder of ArH was condensed to form arene oligomers (*e.g.* Ar-Ar). The arenium ions were identified and quantified by *in situ* ^1H-NMR,[6] while the condensed products were determined following quench and separation by GC, GC-MS, HPLC, and UV techniques. The stability and identity of these arenium ions in this aprotic medium was separately confirmed by a comparison of their integrated ^1H-NMR spectra[7] with those obtained by dissolving the corresponding, independently synthesized heptachlorodialuminate salts[8,9] in neat Ga_2Cl_6. Thus we can represent this oxidation half-reaction by eq. 1

$$4\ ArH \longrightarrow 2\ ArH_2^+ + Ar\text{-}Ar + 2\ e^- \qquad (1)$$

where Ar-Ar represents the oligomerized arenes, collectively. The fact that the yield of

ArH_2^+ substantially exceeded 50% was in accord with the fact that for 1 and 2, at least, the oligomers were, on the average, more highly condensed than the simple bi-aryl shown in eq. (1). In the case of 2, the primary condensed product was anthra[2,1-a]aceanthrylene in which there are two bonds connecting two anthracene rings. Had this been the only product the protons released would have been enough to protonate 67% of the starting material. For the reaction of 1, no predominant condensed product was formed. Several bipyrenes connected by either one or two bonds were identified following HPLC separation by comparison of their UV spectra with those reported in the literature.[10] For the reaction of 3, the extremely low solubility of the condensed products precluded their structural identification.

These arene solutions in molten Ga_2Cl_6 were also examined by ^{71}Ga NMR, and the results demonstrated that the above oxidation reactions were accompanied by the reduction of Ga(III) to form Ga^+.[11] The resonance for the Ga^+ ion in the melt solutions of 1, 2, and 3 was observed at -830 ± 10 ppm relative to $GaCl_4^-$ in 9 M HCl, which is consistent with reported values.[12] The formation of Ga^+ was further substantiated from NMR measurements on Ga_2Cl_6 melts containing Ga^+ that was independently prepared from the reaction of Ga^0 with Ga_2Cl_6. Based on what is known about structural entities in molten chlorogallate(III) systems,[13] we can reasonably assign the fate of the chloride ions during reduction and arrive at eq. 2 for the reduction half-reaction.

$$5\ Ga_2Cl_6 + 2\ e^- \longrightarrow Ga^+ + 3\ Ga_3Cl_{10}^- \qquad (2)$$

The quantitative link between eq. 1 and 2 was forged by quantifying the Ga^+ formed in these oxidation reactions and comparing the result with the amount of ArH_2^+ as determined by ^1H NMR. The quantity of Ga^+ present was determined by comparison of the integral of the ^{71}Ga NMR signal with the integrals obtained from standard solutions of Ga^+ in Ga_2Cl_6. We found that in the oxidation of 1, 2, or 3 the ArH_2^+/Ga^+ mole ratio has the value 2 within an experimental uncertainty of about 10%. Thus the complete redox reaction can be written as shown in eq. 3. It should be noted that the

$$4\ ArH + 5\ Ga_2Cl_6 \longrightarrow 2\ ArH_2^+ + Ar\text{-}Ar + Ga^+ + 3\ Ga_3Cl_{10}^- \qquad (3)$$

key ArH_2^+/Ga^+ ratio that links the oxidation and reduction half-reactions is independent of the nature of the mixture of arene oligomers that are formed.

The oxidative coupling of arenes accompanied by the release of protons, as shown in eq. 3, is a well-known aspect of arene radical cation chemistry.[14] A less common feature of this reaction is the capture of the released protons by the neutral arene to form stable arenium ions in an aprotic medium. However, the same reaction is also known to occur in molten, $SbCl_3$-rich $SbCl_3$-$AlCl_3$ mixtures for the same arenes and at the same temperatures used in the present investigation.[8] In the $SbCl_3$-rich medium the oxidant is Sb(III).

When the reaction products in eq. 3 are quenched in aqueous HCl, Ga(I) is oxidized to Ga(III) in a complex reaction and the arenium ions are largely converted to the parent arene.

It is for this reason that an in situ determination of the oxidized (ArH_2^+) and reduced (Ga^+) products was called for.

Arene 4 is decidedly less oxidizable and less basic than 1, 2, and 3, and it behaved quite differently when dissolved in Ga_2Cl_6. Dilute solutions of 4 gave no ESR signals, while in more concentrated solutions this arene underwent catalytic condensation, hydrogen transfer and cracking reactions like those reported for solutions of 4 in molten $SbCl_3$-10 mol % $AlCl_3$.[15]

This study has demonstrated that molten Ga_2Cl_6 is a moderate oxidant capable of participating in single electron transfer reactions with polycyclic arenes. In view of this result and our earlier discoveries that other molten Lewis acids, such as $SbCl_3$ and $SbCl_3$-$AlCl_3$, are also oxidants for many organic substrates we suggest that the potential role of single electron transfer reactions in the interaction of organic substrates with concentrated Lewis acids deserves more consideration than it is generally afforded.

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References and Notes

(1) E.g., see Eberson, L. Adv. Phys. Org. Chem. 1982, 18, 79.

(2) $GaCl_3$ exists as a chlorine bridged dimer, Ga_2Cl_6, isostructural with Al_2Cl_6.

(3) For example see: (a) Jensen, F. R.; Goldman, G. in "Friedel Crafts and Related Reactions"; G. A. Olah, Ed.; Interscience: New York, 1964; Vol. III, Part 2, p. 1021. (b) Sheka, I. A.; Chaus, I. S.; Mityureva, T. T., "The Chemistry of Gallium"; Elsevier: New York, 1966, p. 269.

(4) Commercial 99.999% anhydrous $GaCl_3$ (Cerac) was further purified by sublimation followed by zone refining. The arenes were commercial reagents of the highest quality (99+ to 99.9+ %) which were further sublimed and/or recrystallized before use. Scrupulous materials handling procedures, including the use of inert atmosphere glove boxes and vacuum-tight reaction vessels, were followed to exclude air and other extraneous oxidizing or protic substances.

(5) For $1^{+\bullet}$, a_1 (4H) = 5.38, a_2 (2H) = 1.21 and a_4 (4H) = 2.14 G. For $2^{+\bullet}$, a_1 (4H) = 3.06, a_2 (4H) = 1.37 and a_9 (2H) = 6.47 G. For $3^{+\bullet}$, a_1 (4H) = 1.70, a_2 (4H) = 1.03 and a_5 (4H) = 5.01 G. These hyperfine splitting constants are very similar to those measured in other solvent systems. See, Buchanan, A. C., III; Livingston, R.; Dworkin, A. S.; Smith, G. P. J. Phys. Chem. 1980, 84, 423.

(6) ^1H NMR spectra were obtained at 200.17 MHz (Nicolet NT-200 spectrometer) with chemical shifts referenced externally to $(CH_3)_4NCl$ (δ 3.12) in Ga_2Cl_6.

(7) The arenium ions of **1**, **2**, and **3** are protonated as expected in the 1-, 9-, and 5-positions, respectively. The observed chemical shifts are similar to those reported for these ions in molten $AlCl_3$-NaCl-KCl (60:26:14 mol %) and $SbCl_3$-$AlCl_3$ (90:10 mol %).[8]

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(11) ^{71}Ga NMR spectra were obtained at 24.26 MHz on a Varian FT-80 spectrometer. No signals were detected for Ga(III) in Ga_2Cl_6 or $Ga_3Cl_{10}^-$, presumably due to excessive quadrupolar broadening associated with the asymmetrical environments of the gallium nuclei in these species.

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(14) For example see: (a) Parker, V. D.; Ronlán, A. *J. Am. Chem. Soc.* **1975**, *97*, 4714. (b) Ronlán, A.; Hammerich, O.; Parker, V. D. *J. Am. Chem. Soc.* **1973**, *95*, 7132. (c) Wen, L.-S.; Kovacic, P. *Tetrahedron* **1978**, *34*, 2723. (d) Parker, V. D. *Acc. Chem. Res.* **1984**, *17*, 243.

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