Title
COMPARISON OF POLYNUCLEAR AROMATIC HYDROCARBON CATION SALTS WITH SALTS OF SIMPLE FLUOROAROMATIC CATIONS

Permalink
https://escholarship.org/uc/item/3cw3v01v

Authors
Richardson, T.J.
Tanzella, F. L.
Bartlett, N.

Publication Date
1987-02-01
Presented at the 192nd National ACS Meeting, Anaheim, CA, September 7-12, 1986, and to be published in Advances in Chemistry Series

COMPARISON OF POLYNUCLEAR AROMATIC HYDROCARBON CATION SALTS WITH SALTS OF SIMPLE FLUOROAROMATIC CATIONS

T.J. Richardson, F.L. Tanzella, and N. Bartlett

February 1987

TWO-WEEK LOAN COPY
This is a Library Circulating Copy which may be borrowed for two weeks

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
COMPARISON OF POLYNUCLEAR AROMATIC HYDROCARBON CATION SALTS WITH SALTS OF SIMPLE FLUOROAROMATIC CATIONS

Thomas J. Richardson, Francis L. Tanzella, and Neil Bartlett

Department of Chemistry, University of California, and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720.

Abstract

Electron oxidation of the fluoro-aromatics \( \text{C}_6\text{F}_6 \) and \( \text{C}_{10}\text{F}_8 \) by \( \text{O}_2^+ \) salts yields salts of the radical cations \( \text{C}_6\text{F}_6^+ \) and \( \text{C}_{10}\text{F}_8^+ \) which are Curie-Law paramagnets. The fluoro-analogs of the "metallic" \( (\text{C}_{10}\text{H}_8)_2^+ \) salts do not exist. Repulsive interactions involving the electron-rich fluorine ligands of the fluoro-aromatics are probably responsible for the failure of these species to make metallic stacks. Attempts to prepare \( \text{C}_6\text{H}_6^+ \) salts have given the poly(paraphenylene) cation salts \( (\text{C}_6\text{H}_4)_n^+\text{AsF}_6^- \) which are good electronic conductors. Electron oxidation of polynuclear aromatics by \( \text{C}_6\text{F}_6^+ \) salts or by \( \text{AsF}_5 \), e.g. \( 3\text{AsF}_5 + 2\text{C}_{24}\text{H}_{12} \rightarrow 2\text{C}_{24}\text{H}_{12}^+\text{AsF}_6^- + \text{AsF}_3 \), yields what appear to be salts of the polynuclear aromatic cations. The magnetic and electrical properties of such salts are described.
Introduction

Radical cation salts derived from hexafluorobenzene (1), octafluorotoluene (2), pentafluoropyridine (3) and octafluoronaphthalene (4) have been known for some time, and some of their reaction chemistry has been discussed in a recent publication.(5) Hexafluorobenzene hexafluoroarsenate, C_{6}F_{6}^{+}AsF_{6}^{-}, has oxidizing power sufficient to electron-oxidize most other mono- and polycyclic aromatics.

Fritz and co-workers (6) have prepared bis(naphthalene) salts, (C_{10}H_{8})_{2}^{+}MF_{6}^{-} (M = P, As) in which the aromatic molecules occur in stacks, resulting in metal-like electrical conductivity ($\sigma = 0.12 \pm 0.046 \Omega^{-1} \text{ cm}^{-1}$ for a polycrystalline pellet). This suggested the possibility of analogous behavior in the fluoroaromatic series. Materials containing dimer cations, however, have not been isolated from reaction mixtures containing excess amounts of the neutral monomers, nor from controlled reduction of mono-cation salts. In each case, the cations are monomeric and magnetically independent of one another.

Attempts to prepare salts containing C_{6}H_{6}^{+} have led to polymerization with HF-elimination, the resulting solid containing electron oxidized poly(paraphenylene).(7)

Thermally stable blue-green powders have been obtained by oxidation of coronene using O_{2}AsF_{6}, C_{6}F_{6}AsF_{6} or AsF_{5}. Infrared spectra of these materials show the presence of the AsF_{6}^{-} ion in addition to the coronene-like cation. Gravimetry and elemental analyses indicate compositions ranging from (C_{24}H_{12})_{4.0}AsF_{6} to
(C₂₄H₁₂)₀.₂₅AsF₆ with at least three crystallographically distinct phases indicated. In the X-ray powder diffraction patterns of these solids very strong reflections with d-spacings of about 3.3 Å suggest that the coronene species may be stacked in plate-like fashion. Crude resistance measurements on pellets of the polycrystalline powders indicate ambient-temperature conductivity for these salts in excess of 1.0 x 10⁻³ Ω⁻¹ cm⁻¹.

Experimental

The syntheses of cation salts of the monocyclic fluoroaromatics and of octafluoronaphthalene have been described elsewhere.(1-5) Manipulations of air- or moisture-sensitive materials were carried out in a Vacuum Atmospheres Dri-Lab or in a stainless steel vacuum line fitted with Teflon FEP (Chemplast, Inc., Van Nuys, CA) or fused silica reaction vessels.

The reaction of benzene with O₇AsF₆. In a typical reaction, benzene (0.403 g, 5.16 mmol) was co-condensed at 77K with sulfuryl chloride fluoride (8 ml) into a Teflon FEP reaction vessel containing O₂AsF₆ (0.912 g, 4.13 mmol, prepared as in Ref. 8). On warming to 195K, a green solution was obtained from which oxygen evolved steadily for a period of fifteen minutes as the color faded. When the solvent and volatile products were removed at room temperature, a dark brown solid (0.893 g) remained. The product was washed with liquid anhydrous hydrogen fluoride to remove (C₆H₅)₂AsF₂AsF₆ formed by the reaction of benzene with AsF₅ present in the reaction mixture due to thermal decomposition
of O₂AsF₆. The resulting brown powder (0.182 g) is diamagnetic, with room temperature conductivity (pressed pellet) in excess of 1.0 x 10⁻² Ω⁻¹ cm⁻¹. Anal. [(C₆H₄)nAsF₆, n = 4.05, based on C:As ratio] C₆H₆AsF₆: calcd, 21.05; found 22.07. The infrared spectrum (Figure 1) of the powder contains absorptions due to oxidized poly(paraphenylene) (9) and the hexafluoroarsenate(V) ion.

The reaction of benzene with C₆F₆AsF₆. C₆F₆AsF₆ was prepared in situ by reacting O₂AsF₆ (0.473 g, 2.14 mmol) with an excess of C₆F₆ in SO₂ClF prior to the addition of benzene (0.323 g, 4.14 mmol). The reaction was complete in one hour at 195K. The product (0.546 g, 0.134 g after washing with HF) was identical to that produced from O₂AsF₆. Elemental analyses of samples from four preparations gave values for n ranging from 1.8 to 4.4. The C:H ratio varied from 3.6 to 4.4 in eight analyzed samples.

The reaction of naphthalene with an excess of AsF₅. Naphthalene (0.20 g, 1.6 mmol) was dissolved in hexafluorobenzene (5 ml) in an evacuated Teflon FEP reactor. AsF₅ was admitted to the vessel at room temperature until a total pressure of 1 atm. was obtained. Copious amounts of a fluffy purple solid precipitated. Anal. C 59.78, H 2.81, C:H ratio 1.77. The solid was amorphous to x-rays.

In another experiment, a small amount of AsF₅ was added slowly to a solution of naphthalene in CH₂Cl₂ (mole ratio of AsF₅ to C₁₀H₈ ca. 1:6). Above the surface of the solution, where an
excess of AsF₅ was present, the purple solid described above was formed. In the solution, however, a much darker, nearly black solid precipitated. Over a period of one to two hours following removal of the solvent, both products became grey. No x-ray pattern could be obtained from these solids.

Oxidation of coronene by O₂AsF₆. O₂AsF₆ (0.342g, 1.55 mmol) was placed in a Teflon FEP reaction vessel. A disc of Teflon filter paper was inserted above the solid, and coronene (0.464g, 1.55 mmol) was placed on the filter. Sufficient SO₂ClF was condensed into the vessel to cover the coronene. At 195K, the reaction proceeded slowly, reaching completion in one hour. The vessel was allowed to warm to room temperature, and volatile products were removed under vacuum after one hour. The product was a green, free-flowing powder. Anal. [(C₂₄H₁₂)₀.₉₇AsF₆] C,H. The infrared spectrum of this solid (Figure 2) contains, in addition to bands similar to those in neutral coronene, characteristic absorptions at ca. 700 and 400 cm⁻¹ due to hexafluoroarsenate (V). The magnetic susceptibility was found to follow the Curie-Weiss Law down to 12K with μ_eff = 0.36 B.M., θ = -1.8°.

Oxidation of Coronene by excess C₆F₆AsF₆. C₆F₆AsF₆ was prepared in situ from O₂AsF₆ (1.0g, 4.5mmol) in SO₂ClF. The reaction vessel was held at 77K in a dry nitrogen-filled glove bag while coronene (0.15g, 0.50mmol) was added. The mixture was warmed to 195K, and the reaction allowed to proceed for 90 minutes. The product, obtained after removal of volatiles at room temperature was a dark-green friable powder. Anal.
[(C_{24}H_{12})_{0.51}AsF_6 \text{C,H.}] The infrared spectrum of this solid (Figure 2c) is similar to the more coronene-rich material described above, but the absorptions due to AsF_6^- are relatively more intense. The magnetic susceptibility exhibits Curie-Weiss behavior down to 6K with $\mu_{\text{eff}} = 0.83$ B.M., $\Theta = -5.9^\circ$.

**Oxidation of coronene by arsenic pentafluoride.** Coronene reacted rapidly to give green and blue-green free-flowing powders on exposure to gaseous AsF_5 in a variety of solvents and at varying AsF_5 partial pressures. Solvents used included sulfuryl chloride fluoride, hexafluorobenzene, dichloromethane, trichlorofluoromethane and 1,1,1-trichlorotrifluoroethane. Arsenic trifluoride was detected as a reaction product by infrared spectroscopy. The color of the solid thus produced seems to be a qualitative measure of the extent of oxidation, the more highly oxidized materials being bluer than the coronene-rich solids. Product compositions were determined by gravimetry, with the assumption that arsenic is present only as AsF_6^- and that coronene is present as neutral molecules or electron-oxidized cations. Observed mole ratios of coronene to hexafluoroarsenate varied widely (4.0 to 0.25), smaller values being associated with the higher concentrations of arsenic pentafluoride. Debye-Scherrer photographs of the polycrystalline powders (Table I) show that the products differ significantly over the composition range and that neutral coronene, if present, is incorporated into the structures and not co-existing as a separate phase.
Results and Discussion

Chemical syntheses of radical cation salts by electron oxidation of neutral aromatic precursors require powerful oxidizing agents and stabilizing anions with high ionization energies (e.g. AsF$_6^-$, ReF$_6^-$, SbF$_6^-$, Sb$_2$F$_{11}^-$). The stable salt of an aromatic cation of sufficient oxidizing strength can be employed as a synthetic reagent in the electron oxidation of other aromatics with lower ionization energies. Thus, hexafluorobenzene hexafluoroarsenate(Ⅴ), C$_6$F$_6$AsF$_6$, provides a convenient one-electron oxidizing agent somewhat less energetic than the dioxygenyl salt (I(O$_2$) = 281 kcal mol$^{-1}$; I(C$_6$F$_6$) = 230 kcal mol$^{-1}$) (10), from which it is most easily prepared:

$$O_2AsF_6 + C_6F_6 \rightarrow O_2 + C_6F_6AsF_6$$  (1)

The reduction product is the relatively inert and volatile hexafluorobenzene molecule. Moreover, the clean decomposition of C$_6$F$_6$AsF$_6$:

$$2C_6F_6AsF_6 \rightarrow C_6F_6 + 1,4-C_6F_8 + 2AsF_5$$  (2)

at room temperature to volatile products (5) means that an oxidation can be carried out using an excess of C$_6$F$_6$AsF$_6$. The remaining oxidant is then allowed to decompose in situ at room temperature and the volatile side-products are removed under vacuum. This technique has been applied in the quantitative
preparation of octafluoronaphthalene hexafluoroarsenate \((I(C_{10}F_8) = 204 \text{ kcal mol}^{-1})\):

\[
C_6F_6AsF_6 + C_{10}F_8 \rightarrow C_6F_6 + C_{10}F_8AsF_6
\]  

(3)

In the two fluoro-aromatic cation salts, the cations appear to be well separated from one another by the anions. In \(C_6F_6AsF_6\), each ion is surrounded by eight nearest neighbors of opposite charge in a distorted CsCl-type lattice. In the case of \(C_{10}F_8AsF_6\), although details of the structure are not yet known, the symmetry and unit cell dimensions seem to preclude an arrangement involving co-planar stacks of cations.

Octafluoronaphthalene hexafluoroarsenate is exceptionally stable (dec. 395K), and in light of the report (6) of conductivity in \((ClOFS)_2PF_6\), we sought to prepare the fluoro-analog of this "synthetic metal". Despite repeated attempts using a variety of approaches, however, we have not obtained such a material. Metallic behavior in partially-charged organic stacks derives from bonding interactions which occur as a consequence of overlapping of the highest occupied molecular orbitals (HOMOs) and singly-occupied molecular orbitals (SOMOs) of the stacked ring systems. This requires that the planar aromatic species be closer together than their van der Waals thickness of about 3.3 Å, as has been observed in \((ClOFS)_2PF_6\). Such a close juxtaposition of octafluoronaphthalene molecules, however would also bring the electron-rich F-ligands close
together. This is probably a sufficiently strongly repulsive interaction to offset the weak bonding interaction between the electron-oxidized and neutral aromatic rings. Attempts to prepare a bis(hexafluorobenzene)$^+$ salt were also unsuccessful. Although arsenic pentafluoride is able to electron oxidize:

$$3\text{AsF}_5 + 2e^- \rightarrow 2\text{AsF}_6^- + \text{AsF}_3$$  \hspace{1cm} (4)

its oxidizing power is weaker than that of C$_6$F$_6^+$. In the case of benzene, AsF$_5$ and C$_6$H$_6$ react quantitatively in HF or SO$_2$ClF (10) to give the colorless crystalline solid (C$_6$H$_5$)$_2$AsF$_2^+$AsF$_6^- $:

$$2\text{C}_6\text{H}_6 + 2\text{AsF}_5 \rightarrow (\text{C}_6\text{H}_5)_2\text{AsF}_2^+\text{AsF}_6^-$$ \hspace{1cm} (5)

With O$_2^+$ or C$_6$F$_6^+$, however, benzene reacts to give poly-(paraphenylene) derivatives. While polymerization is never observed in the AsF$_5$ reaction, some of the diphenylarsonium salt is always formed in the O$_2^+$ and C$_6$F$_6^+$ reactions due to the presence in the reaction mixture of arsenic pentafluoride formed in the decomposition of the oxidizing agents. This suggests that the first step toward polymerization is electron oxidation of C$_6$H$_6$ ($I = 212$ kcal mol$^{-1}$) to C$_6$H$_6^+$, and that AsF$_5$ is not able to achieve this oxidation:

$$\text{C}_6\text{H}_6 + \text{C}_6\text{F}_6^+ \text{ (or O}_2^+\text{)} \rightarrow \text{C}_6\text{H}_6^+ + \text{C}_6\text{F}_6 \text{ (or O}_2).$$  \hspace{1cm} (6)
Subsequent abstraction of $H^+$ by the anion may also occur:

$$C_6H_6^+ + AsF_6^- \rightarrow [C_6H_5]^+ + HF + AsF_5.$$  (7)

Such interpretations are consistent with the conclusions of other investigators as to the cationic nature of intermediates in the preparation of poly(paraphenylene). (11,12,13) As the number of fused or linked rings in a series of polynuclear aromatic molecules increases, the ionization energies of the neutral molecules decreases ($I$(biphenyl) = 183 kcal mol$^{-1}$, $I$(terphenyl) = 181 kcal mol$^{-1}$; $I$(naphthalene) = 187 kcal mol$^{-1}$, $I$(anthracene) = 171 kcal mol$^{-1}$, $I$(naphthacene) = 161 kcal mol$^{-1}$).

The polymer which results when benzene is reacted with the powerful oxidizers $O_2^+$ and $C_6F_6^+$ is readily oxidized by $AsF_5$ (14,15) (which reagent, although not capable of initiating the polymerization of benzene, can polymerize the more easily oxidized phenylene oligomers, even including biphenyl).

While the aromatics undergo hydrogen elimination readily upon oxidation (benzene(16) and naphthalene(17) can be polymerized electrochemically; binaphthyl is formed in the thermal decomposition of bis(naphthalene) hexafluorophosphate), the analogous elimination of $F^+$ in the fluoro-aromatics is not energetically feasible.

For large, planar fused-ring systems, the tendency toward co-planar stacking gives rise to behavior similar to that observed for graphite intercalation compounds. Coronene is
rapidly oxidized by dioxygenyl hexafluoroarsenate, hexafluorobenzene hexafluoroarsenate, or arsenic pentafluoride:

\[
\text{nC}_{24}\text{H}_{12} + \text{O}_2\text{AsF}_6 \rightarrow (\text{C}_{24}\text{H}_{12})_n^+\text{AsF}_6^- + \text{O}_2
\] (8)

\[
\text{nC}_{24}\text{H}_{12} + \text{C}_6\text{F}_6\text{AsF}_6 \rightarrow (\text{C}_{24}\text{H}_{12})_n^+\text{AsF}_6^- + \text{C}_6\text{F}_6
\] (9)

\[
2\text{nC}_{24}\text{H}_{12} + 3\text{AsF}_5 \rightarrow 2(\text{C}_{24}\text{H}_{12})_n^+\text{AsF}_6^- + \text{AsF}_3
\] (10)

The extent of oxidation and, thus, the observed stoichiometry varies widely in the materials prepared by oxidation of coronene. The x-ray diffraction patterns of these solids are characteristic of the particular stoichiometries, but they have common features, the most striking being the presence in each pattern of a strong reflection with a d-spacing of about 3.3 Å, the thickness of a coronene molecule. This suggests the possibility that these are layered materials with the anions occupying positions within the layers.

\[\text{H}^+\text{-elimination} \] cannot be ruled out in the syntheses of the coronene derivatives described above, or for any other aromatic system. Although the materials reported here appear to be homogeneous and non-polymeric, containing arsenic only as \(\text{AsF}_6^-\), the magnetic susceptibility data are not easily explained in terms of purely ionic formulations. The observed electrical conductivity may, therefore, be due either to stacking of the cations or to linking through HF elimination at the edges of the
planar ring systems, or to a combination of the two. Clearly, the structures adopted by these materials are strongly influenced by the extent of oxidation and the sizes and number of anionic species present.

Conclusions

Electron-oxidation of fluoro-aromatic molecules produces mono-cationic salts whose thermal decomposition products are monomeric and result from disproportionation and auto-oxidation. The more strongly oxidizing salts, in particular $C_6F_6AsF_6$, can be used as synthetic reagents in the preparation of other radical cation salts. Whereas the fluoro- cation salts contain single molecular cations with no apparent tendency for overlap of one cation with another, aromatic cation salts display a range of stoichiometries and structures in which cation-cation or cation-molecule interaction is favored. The aromatics also exhibit a tendency toward polymerization, resulting in chain polymers which are more readily oxidized than their monomer precursors to become electrical conductors.

Acknowledgments

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
REFERENCES


Table I. X-ray Powder Diffraction Data (d-spacings) for Coronene Salts: $(C_{24}H_{12})_n\text{AsF}_6$

(w = weak, s = strong, m = medium, v = very)

<table>
<thead>
<tr>
<th>n</th>
<th>Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51</td>
<td>10.92w, 9.52m, 8.63vw, 7.57ms, 6.96s, 6.53s, 6.10w, 5.64w, 5.28s, 4.93m, 4.70m, 4.51vs, 4.44m, 3.98s, 3.52m, 3.33vs, 3.19w, 3.07vw, 2.78m</td>
</tr>
<tr>
<td>0.89</td>
<td>12.42mw, 10.89w, 8.54m, 7.09vs, 6.49m, 6.08m, 5.43s, 5.14m, 4.79w, 4.58vvs, 4.36m, 4.17vw, 4.03m, 3.71vw, 3.54mw, 3.45mw, 3.35vs, 3.21s, 3.01w, 2.87w, 2.15w, 1.65w</td>
</tr>
<tr>
<td>1.88</td>
<td>14.37w, 10.86ms, 7.54vs, 7.04m, 6.54vs, 5.31vs, 4.94vs, 4.67w, 4.35s, 4.19s, 4.02s, 3.72w, 3.61w, 3.50w, 3.32vvs, 3.16w, 2.33w, 1.66vw</td>
</tr>
<tr>
<td>4.00</td>
<td>10.78w, 9.49s, 7.58vs, 6.47vs, 5.97vw, 5.25s, 5.11mw, 4.91w, 4.72w, 4.35s, 3.95s, 3.51s, 3.43m, 3.31vs, 3.20w, 3.16w, 3.06m, 2.77w, 2.66vw, 2.33m, 2.05vw, 1.96vw, 1.90w, 1.65vw, 1.47w</td>
</tr>
</tbody>
</table>
Figures

Figure 1. Infrared spectrum of oxidized poly(paraphenylene).

Figure 2. Infrared spectra of coronene and coronene salts.
INFRARED SPECTRUM OF OXIDIZED POLYPARAPHENYLENE
INFRARED SPECTRA OF CORONENE AND CORONENE SALTS

a) Coronene; b) \((C_{24}H_{12})_nAsF_6\); \(n = 0.97\); c) \((C_{24}H_{12})_nAsF_6\); \(n = 0.51\)

XBL 869-3286
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.