Organometallic Distonic Ions: $^{+}FeC_6H_4^{\bullet}$

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Our continuing investigation of gas phase ion−molecule chemistry involving metal ions[1] has led us to examine the nature and behavior of organometallic ion radicals of a sort that would represent a new class of distonic ions. Distonic ions, with spatially separated charge and radical sites, have been the focus of great interest over the last decade.[2] Often of surprising stability, distonic ions offer the possibility of studying radical reactivity in the gas phase using the charge site as a means of detecting and isolating the radical and its products through the course of a reaction sequence.

As a starting point, prompted by the synthesis of $^{+}P(OCH_3)_3C_6H_4^{\bullet}$ and related distonic ions by Smith and Kenttämaa[3] and by the study of the metal ion complexes Fe(phenyl)$^{+}$ and Fe(*o*-benzyne)$^{+}$ in this laboratory,[4,5] we generated a radical cation, $^{+}FeC_6H_4^{\bullet}$. Reacting laser-desorbed Fe^{+} with 1,4-diiodobenzene yields the 1-Fe-4-iodobenzene cation, $FeC_6H_4I^{+}$, which then loses $I^{\bullet}$ during sustained off-resonance irradiation (SORI)[6] excitation to generate Fe(*p*-benzyne)$^{\bullet+}$ (Scheme 1 and Figure 1a−c). Selected ion−molecule reactions distinguish Fe(*p*-benzyne)$^{\bullet+}$ from its isomer Fe(*o*-benzyne)$^{+}$. Both experiment and theory strongly support the view that this new radical cation is an organometallic distonic ion, $^{+}FeC_6H_4^{\bullet}$.

All of the experiments were performed on an Extrel FTMS-2000 dual cell Fourier transform ion cyclotron resonance mass spectrometer equipped with a 3 T superconducting magnet.[7] Fe^{+} was generated by laser desorption−ionization of the pure metal target using a Nd:YAG laser.[8] 1,4-Diiodobenzene, a solid sample, was introduced into the analyzer side of the dual cell at a pressure of $\sim(0.8-1) \times 10^{-7}$ Torr through a Varian leak valve accompanied by heating the sample and inlet system to $\sim$70−100 °C. Background argon, kept at $\sim 5.0 \times 10^{-6}$ Torr, served as the collision gas[9] for thermalization and for SORI.[6] Other chemicals were pulsed into the cell via General Valve Corp. Series 9 solenoid pulsed valves.[10] The ion isolation was accomplished by using swept double resonance ejection pulses[11] and SWIFT excitation pulses.[12]

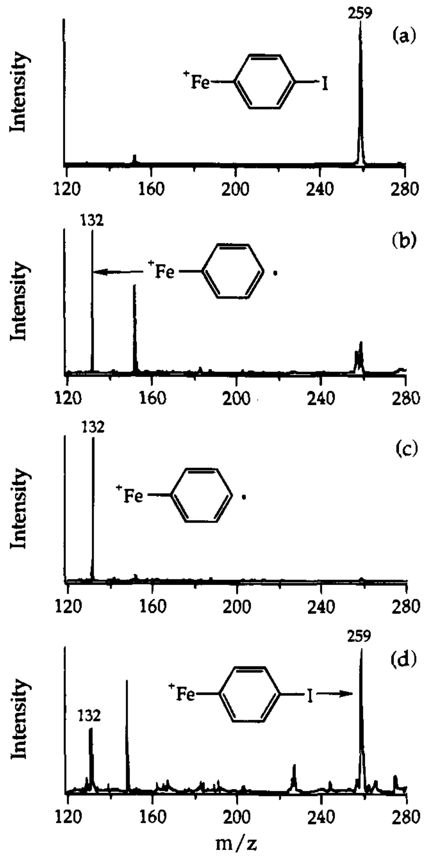
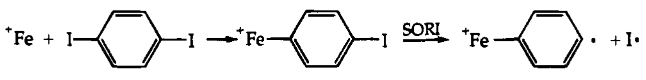


Figure 1. (a) $FeC_6H_4I^{+}$ from the reaction of Fe^{+} with 1,4-diiodobenzene. (b) SORI on $FeC_6H_4I^{+}$ to generate the distonic ion $^{+}FeC_6H_4^{\bullet}$. (c)Isolation of $^{+}FeC_6H_4^{\bullet}$ using ion ejection techniques. (d)$^{+}FeC_6H_4^{\bullet}$ abstracts $I^{\bullet}$ from allyl iodide to yield $FeC_6H_4I^{+}$.

Scheme 1



Fe(*p*-benzyne)$^{\bullet+}$ and Fe(*o*-benzyne)$^{+}$ can be readily distinguished on the basis of their reactivity with dimethyl disulfide,[13] dimethyl diselenide,[3] ethyl chloride, and allyl iodide. Dimethyl disulfide and dimethyl diselenide have been shown to be good indicators of distonic ions, transferring $^{\bullet}SCH_3$ and $^{\bullet}SeCH_3$, respectively, to the radical site of many organic distonic ions.[3,13] Although dimethyl disulfide is observed to react with Fe(*p*-benzyne)$^{\bullet+}$ exclusively by charge exchange, indicating that the corresponding neutral has an ionization potential greater than IP(dimethyl disulfide) = 7.4 eV,[14] the characteristic transfer of $^{\bullet}SeCH_3$ from dimethyl diselenide to this distonic cation is observed. In contrast, only a trace amount of charge transfer is observed for Fe(*o*-benzyne)$^{+}$ reacting with dimethyl disulfide, and no $^{\bullet}SeCH_3$ abstraction is observed with dimethyl diselenide under otherwise identical conditions. The reaction of Fe(*p*-benzyne)$^{\bullet+}$ with ethyl chloride yields four products, $FeC_8H_8Cl^{+}$, $FeC_8H_8^{+}$, $C_8H_9^{+}$, and $C_8H_8^{\bullet+}$, while Fe(*o*-benzyne)$^{+}$ yields three products,[5] $FeC_6H_6^{+}$, $FeC_8H_8^{+}$, and $FeC_6H_5Cl^{+}$, eliminating the possibility that either ion population exists as a mixture of both isomers. Finally, allyl iodide was studied since it has a low homolytic C−I bond dissociation energy (40.7 kcal/mol)[14]

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and since iodine atom abstraction is commonly observed for other radicals upon reaction with allyl iodide.[2] Reaction of allyl iodide with Fe(p-benzyne)$^{\bullet+}$ yields the I$^{\bullet}$ abstraction product, $FeC_6H_4I^+$ (Figure 1d), while the corresponding reaction is not observed with Fe(o-benzyne)$^+$.

Three reaction pathways, which are analogous to those for non-metal-containing distonic ions,[2] may be postulated to account for the observed products. In the first, the charged metal site acts as the activation center, initiating the reaction and in some cases playing the same role as in the Fe(o-benzyne)$^+$ complex, yielding isomolecular products. Charge transfer to dimethyl disulfide and formation of $FeC_8H_8^+$ from ethyl chloride are proposed to follow this reaction pathway. In the second pathway, both sites participate in the reaction. Formation of $C_8H_8^{\bullet+}$ and $C_8H_9^+$ from ethyl chloride may arise in this manner. In the third pathway, the radical site is the only reactive center, initiating the radical abstraction that involves bond formation at the radical site. Abstraction of $^{\bullet}CH_2CH_2Cl$ (or $CH_3CH^{\bullet}Cl$) from ethyl chloride to form $FeC_8H_8Cl^+$, of I$^{\bullet}$ from allyl iodide to form $FeC_6H_4I^+$, and of $^{\bullet}SeCH_3$ from dimethyl diselenide to form $FeC_6H_4SeCH_3^+$ proceeds by this pathway. None of these abstraction products are observed with Fe(o-benzyne)$^+$.

Three structures were treated theoretically: Fe(o-benzyne)$^+$, Fe(m-benzyne)$^{\bullet+}$, and Fe(p-benzyne)$^{\bullet+}$. The geometries were optimized, and vibrational frequencies were computed using density functional theory. The DFT calculations used the B3LYP hybrid functional[15] and were performed using Gaussian-92/DFT.[16] The vibrational frequencies were used to compute the zero point energies and confirm that the structures correspond to minima. Both quartet and sextet states were considered.

The most stable structure is found to be Fe(o-benzyne)$^+$ among the three Fe(benzyne)$^+$ isomers (ortho, meta, and para), where the Fe^+ inserts into the in-plane C−C bond to form a three-membered ring, as previously reported.[17] The meta and para structures have very similar energies and are 26.8 and 27.7 kcal/mol above the ortho one, respectively. These structures correspond to an Fe^+-C single bond, with open shell electrons on both the Fe^+ and the meta or para carbon atoms. The meta and para isomers have quartet ground states, with the lowest sextet states lying 1.10 and 4.95 kcal/mol higher in energy, respectively.

The bond dissociation energy D(Fe$^+$−o-benzyne) = 76 ± 10 kcal/mol has been previously determined.[5a] While we do not measure the bond energy of Fe^+ to the p-benzyne directly, a reasonable estimate is derived by assuming that it is equal to D(Fe$^+$−phenyl) = 71 ± 5 kcal/mol.[4] Alternatively, using D(Fe$^+$−phenyl) = 71 ± 5 kcal/mol, together with $D(C_6H_5-H)$ = 113.5 ± 0.5 kcal/mol[18] from benzene as an estimate for abstracting the para-H and a recently reported value of D(p-C_6H_4−H) = 108.7 ± 3.0 kcal/mol,[18] yields D(Fe$^+$−p-benzyne) = 66 ± 9 kcal/mol. A bond energy estimate can also be obtained by combining the theoretical differential energies discussed above with the recently reported values of ΔH_f for o-, m-, and p-benzyne of 106.6 ± 3.0, 121.9 ± 3.1, and 137.8 ± 2.9 kcal/mol,[18] respectively. A simple calculation indicates that compared to o-benzyne, m-benzyne has a lower bond energy by 12 kcal/mol, while p-benzyne has a higher bond energy by 4 kcal/mol. Finally, from D(Fe$^+$−o-benzyne) = 76 ± 10 kcal/mol, this yields D(Fe$^+$−m-benzyne) = 64 ± 10 kcal/mol and D(Fe$^+$−p-benzyne) = 80 ± 10 kcal/mol, respectively. Given the substantial error bars, these bond energies are in good agreement with the theoretical calculations, which yield 77.6 kcal/mol for the ortho, 69.1 kcal/mol for the meta, and 73.3 kcal/mol for the para isomers, respectively.

The results reported here represent the first evidence of an organometallic distonic ion in the gas phase. Although all of the reactions observed for Fe(p-benzyne)$^{\bullet+}$ may be rationalized as originating from three reaction pathways, the detailed mechanisms of the reactions are still unknown and are under further investigation.

This preliminary study reveals a whole new area of organometallic ion chemistry. In addition to the usual metal center initiated reactions, the radical site may operate either separately or in concert with the metal center to open new reaction pathways.

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