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Identification of Photogenerated Intermediates by Electrospray Ionization Mass Spectrometry

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Electrospray ionization mass spectrometry (ESI-MS) has revolutionized the characterization of nonvolatile substances such as high molecular mass biomolecules and ionic transition metal complexes.[1] This soft ionization technique allows the transfer of ions from solution to the gas phase with little fragmentation, thus simplifying interpretation of the mass spectrum. ESI-MS also offers the possibility of trapping and identifying short-lived intermediates, because bimolecular processes involving ionic species in solution are greatly attenuated when the ions pass into the gas phase.[2]

In this report, we employ ESI-MS to probe the solution photochemical behavior of [CpFebz]PF$_6$, where Cp is η^5-cyclopentadienyl and bz is η^6-benzene. Practical interest in this and other members of the [CpFe(η^6-arene)]$^+$ family arises from their use as visible-light-sensitive photoinitiators for the polymerization of epoxides[3] and other monomers.[4] Mechanistic studies by several groups have established key features of the solution photochemistry of these mixed-ring sandwich complexes.[5] In brief, ligand-field photoexcitation induces loss of arene to produce [CpFe(L)$_3$]$^+$ (eq 1), where L can be solvent or any other potential ligand present in solution. When L is weakly coordinating, the primary photoproduct is unstable and decomposes in a secondary thermal reaction (eq 2). Considerably less certain, however, is the identity of the photogenerated species actually responsible for initiating polymerization in systems containing a monomer. It has been suggested that [CpFe(monomer)$_3$]$^+$ plays this role,[3] but neither it nor any polymeric products containing the CpFe$^+$ unit have been observed. Accordingly, we undertook the present study to identify the active initiator formed upon irradiating [CpFebz]PF$_6$ in the presence of an epoxide and to monitor the first steps in the ensuing polymerization process.

$$\mathrm{CpFe}(\eta^6\text{-arene})^+ \xrightarrow[\mathrm{L}]{h\nu} \mathrm{CpFe(L)_3}^+ + \text{arene} \qquad (1)$$

$$2\mathrm{CpFe(L)_3}^+ \rightarrow \mathrm{Fe(L)_6}^{2+} + \mathrm{FeCp_2} \qquad (2)$$

All ESI-MS experiments were performed in the positive ion mode on a PerSeptive Biosystems Mariner workstation, an apparatus that combines a time-of-flight mass spectrometer with an electrospray source.[6] An optically transparent nanospray tip was fabricated from fused silica tubing (100 μm i.d.). The tip was drawn to a fine point (10−20 μm i.d.) at the spray-delivery end and connected at the other end to a syringe pump. Solutions containing 30−70 μM[7] [CpFebz]PF$_6$ were irradiated directly in the tip by an optical fiber that delivered 488-nm light from an argon ion laser. Because the same photoproducts were obtained over a range of laser intensities, multiphoton excitation and secondary photolysis processes were unimportant. The distance, *D*, between the midpoint of the irradiated zone and the tip end, could be varied by adjusting the position of the fiber with a precision translation stage. With $D = 1.7$ mm and flow rates of 20−80 μL/h, photoproducts required <100 ms to arrive at the tip end for spraying. Literature procedures were followed in the synthesis of [CpFebz]PF$_6$.[8] Cyclohexene oxide was purified by fractional distillation under reduced pressure, and solvents were dried over calcium hydride and distilled prior to use.

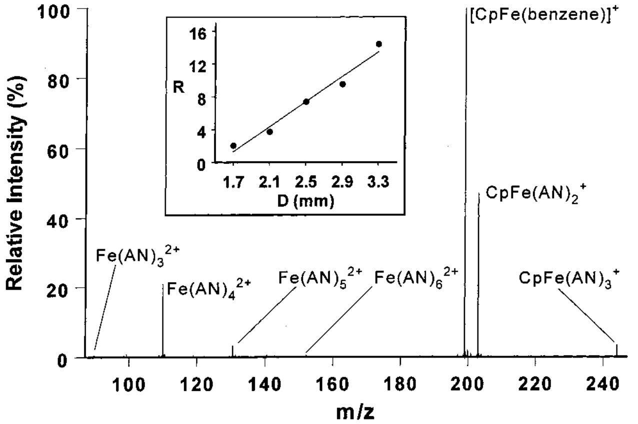

Figure 1. Electrospray ionization mass spectrum of photolysis products from a 70 μM solution of [CpFebz]$^+$ in acetonitrile (AN). Inset: Plot of product ratio, $R = \sum(I_{\mathrm{Fe(AN)}_n{}^{2+}})/\sum(I_{\mathrm{CpFe(AN)}_n{}^{+}})$, vs *D*, the distance of the laser beam from the nanospray tip end.

Control experiments confirmed that [CpFebz]$^+$ emerges unchanged from the nanospray tip in the absence of light. Irradiation of an acetonitrile (AN) solution of the complex in the tip generated two major series of ionic products: [CpFe(AN)$_{1-3}$]$^+$ and [Fe(AN)$_{3-6}$]$^{2+}$ (Figure 1). The first series reflects the photodissociation of benzene (eq 1), while the second series arises from the subsequent thermal loss of the cyclopentadienide anion (eq 2). The coordinatively unsaturated species observed within each series (e.g., five-coordinate [CpFe(AN)$_2$]$^+$ and four-coordinate [Fe(AN)$_4$]$^{2+}$) most likely resulted from collisionally

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(6) Typical operating conditions follow: spray tip potential, 1.9 kV; nozzle potential, 60 V; nozzle temperature, 150 °C; first skimmer potential, 11.5 V; quadrupole temperature, 90−150 °C.

(7) At these low concentrations, ion pairing between [CpFebz]$^+$ and its PF$_6$$^-$ counterion is negligible.[5b]

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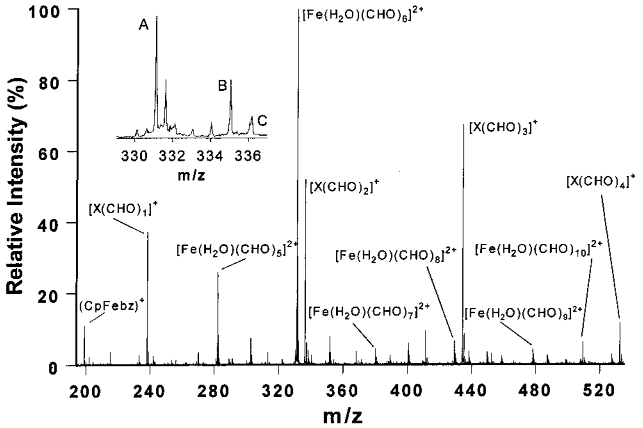


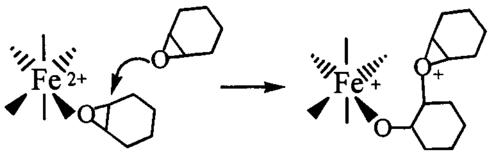
Figure 2. Electrospray ionization mass spectrum of photolysis products from a 1,2-dichloroethane solution containing 41 μM $[CpFebz]^+$ and 40 mM cyclohexene oxide (CHO); distance of laser beam from tip end $D = 8$ mm. Inset: Representative members of three product series observed at $D \sim 0.5$ mm. A = $[(H_2O)Fe(CHO)_6]^{2+}$; B = $[(H_2O)CpFe(CHO)_2]^+$; C = $[X(CHO)_2]^+$.

induced dissociation of AN from $[CpFe(AN)_3]^+$ and $[Fe(AN)_6]^{2+}$ in the region following the first skimmer. Consistent with this explanation, we observed that increasing the kinetic energy of the electrosprayed ions by raising the skimmer voltage favored the production of species with fewer coordinated AN molecules. The parent−offspring relationship between $[CpFe(AN)_3]^+$ and $[Fe(AN)_6]^{2+}$ is evident from the response of the product ratio, $R = \sum(I_{Fe(AN)n^{2+}})/\sum(I_{CpFe(AN)n^+})$,[9] to changes in D (inset to Figure 1). Increasing D at a constant flow rate lengthens the time that $[CpFe(AN)_3]^+$ spends in solution before exiting the spray tip. Consequently, thermal decomposition of this primary photoproduct to $[Fe(AN)_6]^{2+}$ (eq 2) becomes increasingly important and results in the observed trend toward larger R values.

Photolysis of $[CpFebz]^+$ in AN solutions containing 40−400 mM cyclohexene oxide (CHO) yielded the same products observed in pure AN (refer to Figure 1), as well as a few new species. At high CHO concentrations, we detected $[Fe(AN)_3(CHO)]^{2+}$ and $[Fe(AN)_4(CHO)]^{2+}$ but found no products containing more than one epoxide molecule. The latter result indicates that the poorly coordinating CHO does not compete effectively with AN for binding sites about Fe(II). Another product, X^+ ($m/z = 140$), has not yet been identified, but an analysis of isotope patterns has established that it does not contain iron. At high CHO concentrations, a species corresponding to $[X(CHO)]^+$ was detected.

Irradiating $[CpFebz]^+$ and CHO in the poorly coordinating solvent, 1,2-dichloroethane (DCE), yielded a rich vein of new products. With $D \geq 1.7$ mm, we observed two main series: $[(H_2O)Fe(CHO)_{4-12}]^{2+}$ and $[X(CHO)_{0-5}]^+$ (Figure 2). A third series, $[(H_2O)CpFe(CHO)_{1-4}]^+$ (inset to Figure 2), appeared with $D < 0.5$ mm. This behavior indicates that $[(H_2O)CpFe(CHO)_n]^+$ possesses a short lifetime (<50 ms) in solution and only can be observed when generated near the tip end. Recall that a similar situation exists for $[CpFe(AN)_3]^+$ (inset to Figure 1). The water present in the Fe-containing products most likely originated from traces of moisture introduced to the rigorously dried solvent during sample preparation and/or present in the ambient atmosphere at the electrospray tip exit. Signals corresponding to the water-free products, $[Fe(CHO)_{5-8}]^{2+}$ and $[CpFe(CHO)_{1-5}]^+$, also appeared in the mass spectrum, but with diminished intensities.[10]

It is unlikely that all of the molecules present in the heavier Fe-containing products (e.g., $[(H_2O)Fe(CHO)_{12}]^{2+}$, $[Fe(CHO)_8]^{2+}$, and $[CpFe(CHO)_5]^+$) are bound directly to the metal, because the dipositive metal rarely exhibits coordination numbers above six.[11] Accordingly, we have considered two alternative models to describe the structures of these species.[12] Common to each model is the assumption that the metal forms up to six strong coordinate-covalent bonds to ligands in its first coordination sphere. In the *cluster model*, the remaining molecules reside on the periphery as a kind of "solvation shell" held by weaker ion−dipole forces. Many examples of such van der Waals clusters of solvent molecules surrounding a cationic core have been reported.[13] Nonetheless, we discount this model in our system on grounds that similar clusters are absent in samples electrosprayed from AN (see Figure 1), a solvent possessing a larger dipole moment than that of CHO (3.92 vs 2.08 D[14]). In the *polymer model*, a coordinated CHO monomer undergoes nucleophilic attack by the oxygen atom of an uncoordinated monomer unit (eq 3).[15] The ensuing C−O bond formation opens the strained three-membered ring and creates another cationic site for continued chain growth. According to this model, which accommodates all of our experimental observations, products such as $[(H_2O)Fe(CHO)_{12}]^{2+}$, $[Fe(CHO)_8]^{2+}$, and $[CpFe(CHO)_5]^+$ contain a growing polymer chain bound directly to the metal center. In essence, the ESI-MS technique has allowed us to observe the first few steps in the polymerization of an epoxide initiated by cationic iron species. The observation that X^+ forms products containing up to five CHO units also is consistent with the polymer model, and we tentatively propose that this non-iron species is an active initiator for epoxide polymerization.



(3)

In summary, this study has demonstrated that ESI-MS can be a powerful technique for probing the mechanisms of photoinitiated reactions in solution. For the example of $[CpFebz]^+$ in epoxide-containing solutions, our results constitute the first direct support for earlier proposals that photogenerated $[CpFe(epoxide)_3]^+$ is involved in initiating polymerization.[3] Moreover, we have provided evidence for the involvement of at least two other initiating species: Fe^{2+} complexes that result from the thermal decomposition of $[CpFe(epoxide)_3]^+$, and a non-iron containing species, X^+. Accordingly, the roles of several cationic species should be considered in future mechanistic discussions of photoinitiated epoxide polymerization involving $[CpFe(\eta^6\text{-arene})]^+$ complexes.

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[9] The symbol I denotes the relative intensity of a mass spectral peak, and the summation extends over all ions in a series.

[10] Very weak signals corresponding to Fe-containing products containing two, three, and even four water molecules could be detected (e.g., $[(H_2O)_2Fe(CHO)_{11}]^{2+}$, $[(H_2O)_3Fe(CHO)_9]^{2+}$, and $[(H_2O)_4Fe(CHO)_2]^{2+}$).

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