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Investigating reduced metal species via sequential ion/ion and ion/molecule reactions: The reactions of transition metal phenanthrolines with allyl iodide

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ABSTRACT

Sequential ion/ion and ion/molecule reactions are demonstrated in a linear ion trap mass spectrometer and are used to probe the reactivity of metal complexes in unusual ionization states. Taking advantage of the instrument's electron transfer dissociation (ETD) capabilities, the mono- and bis-phenanthroline complexes of Fe(I), Co(I), Ni(I), Cu(I), and Zn(I) were formed by reduction of the corresponding M(II) species in an ion/ion reaction with the fluoranthene radical anion. The chemistry of the M(I) species was probed in ion/molecule reactions with allyl iodide. The bis-phenanthroline complexes generally give slow reactions and the metals were oxidized to M(II) iodide complexes with presumably the release of allyl radicals. The mono-phenanthroline complexes are much more reactive and give M(II) iodide complexes, M(II) allyl complexes, and adducts. The overall reactivity is in accord with density functional theory calculations and mirrors that of proposed intermediates in condensed-phase catalytic cycles.

1. Introduction

Ion/ion reactions have been widely studied in recent years because they offer novel ways to gain structural information about analytes, particularly complex biological molecules [1–4]. Although many approaches have been used, the one-electron reduction of analytes with the fluoranthene radical anion has been incorporated into commercial instrumentation and was been widely employed in peptide fragmentation schemes (commonly referred to as electron transfer dissociation, ETD) [3]. This methodology has much in common with electron-capture dissociation [5], but can be applied in situations where reactions with low-energy electrons are not practical. Although it is not as common, ion/ion reactions employing anions with weakly-bound electrons can also be used to generate species in novel oxidation states via the selective one-electron reduction of precursor ions. In ion-trap mass spectrometers, the trapping potentials make it feasible to conduct ion/ion or ion/molecule reactions. With appropriate reagent pressures and trapping sequences, it is possible to create hybrid experiments in these instruments that link together ion/ion, ion/molecule, and potentially collision-induced dissociation processes. In the current study, we demonstrate the ability to complete ion/ion followed by ion/molecule reactions in a modified, commercial linear ion trap mass spectrometer with ETD capabilities. The results suggest that this is a general way of studying the bimolecular chemistry of species in unusual oxidation states.

During a variety of reduction processes, metals pass through uncommon oxidation states. In many cases, it is difficult to isolate and study the metals in these oxidation states, but it is believed that they can engage in useful and interesting chemical reactivity. To establish a method for examining these types of systems, we have initially focused on phenanthroline complexes of transition metals in the +1 oxidation state (Scheme 1). Specifically, we have examined the mono- and bis-phenanthroline complexes of Fe(I), Co(I), Ni(I), Cu(I), and Zn(I). Aside from copper, each of these metals is typically not found in the +1 oxidation state. Mestdagh and Rolando have examined related bare metal cation species and their reactivity with allyl chloride [6]. Phenanthroline provides a rigid, bidentate ligand and the properties of phenanthroline metal complexes have been widely explored in the past in the condensed and gas phase [7–9]. In the present context, we view them as ideal models for testing our system for completing ion/ion followed by ion/molecule reactions. It should be noted that McLuckey [10,11] has used metal phenanthroline complexes in the past in ion/ion reactions. However in those studies, the metal phenanthrolines

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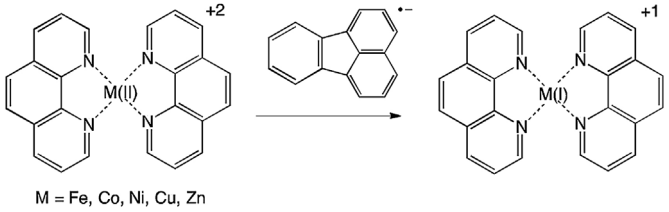

Scheme 1. Reactant ions.

were used to oxidize poly-anions of interest and the bimolecular chemistry of the reduced metal complex was not explored.

For these metals, complexes of the +1 oxidation state are expected to be active as reducing agents and can play roles in the reductive cleavage of carbon-halogen bonds. In addition, there has been recent interest in C—C coupling processes involving Ni(I), Co(I), and Fe(I) [12–16]. For example, Norrby has shown that it is an Fe(I) species that undergoes the rate-determining oxidative addition in an iron-catalyzed coupling reaction [12]. These species also are transients in the electrochemical reduction/oxidation of metals and can undergo unusual chemistry near electrodes [17–22]. Here we will focus on the reactions of M(I) phenanthroline species with allyl iodide.

2. Methods

All experiments were performed in a modified Thermo Electron LTQ XL^{TM} linear quadrupole ion trap mass spectrometer with an electrospray ionization source (ESI). The modifications allow for the introduction of reagent gases into the helium buffer gas and are similar to those we have made to Finnigan LCQ ion trap mass spectrometers in the past [23,24]. The metal complexes were generated via ESI from 10^{-5} M solutions of an appropriate metal salt and 1, 10-phenanthroline. Flow rates ranging from 5 to 10 μL/min were used with typically an ESI needle voltage of 5 kV.

The neutral reagents were introduced into the linear quadrupole as part of the helium buffer gas flow. A consistent and constant flow of the neutral reagent was added by a syringe pump (30–140 μL/h) to a measured flow of helium (1–1.5 L/min). Rapid vaporization of the liquid reagent at the needle tip allows for molar mixing ratios of ~10^3–10^5 He/reagent. The majority of the neutral reagent gas mixture exits the manifold through a flow meter; however a small amount is drawn into the mass analyzer cavity (~1 mL/min) through the "open split" restrictor capillary. The pressure created by the reagent can be calculated from helium pressure (~10^{-3} torr) and the mixing ratio (taking into account differential diffusion) [24]. The system is regularly calibrated using reactions with known rate constants [25].

In a typical experiment, the metal complex solution is introduced via the ESI interface. The system is tuned to the peak of interest and then this species is isolated in the ion trap. Electron transfer dissociation (ETD) is performed on the isolated dication, resulting in a reduced, singly charged complex. The newly reduced complex is then isolated again in the ion trap. Once a suitable, steady signal has been established, the neutral reagent mixture is introduced into the helium mixing manifold. The system is allowed to equilibrate for several minutes. The LTQ software is set for tandem mass spectrometry (MS/MS) scans of the singly-charged ion, but with an excitation energy of 0 V. The reactions were monitored and data was collected as a function of reaction time at various neutral reagent flow rates (reagent pressures). All kinetic measurements were performed under the assumption of pseudo first-order conditions. This assumption is made because the neutral reagent concentration is much greater than the ion concentration (reagent/cation = 10^5–10^6). The reagent flow rates are chosen to produce kinetic runs that cover two to three half-lives. All reported rates are measured at three different flow rates and at least 10 kinetic runs were collected on two or more days. The kinetic plots showed linearity with correlation coefficients (r^2) greater than 0.95. No corrections are incorporated for possible mass discrimination in branching ratios. We have shown in the past that the ion trap provides a reaction environment at near thermal temperatures [23].

All reagents were purchased from commercial sources and were used with no further purification. The following salts were used in preparing the complexes: cobalt (II) chloride (Acros, Geel, Belgium), copper(II) acetate (Fisher, Pittsburgh, PA), iron(II) chloride (Mallinckrodt, St. Louis, MO), nickel (II) acetate tetrahydrate (Sigma, St. Louis, MO), and zinc (II) chloride (Sigma, St. Louis, MO). The ligand solution consisted of 1,10-phenanthroline (Sigma, St. Louis, MO). Density functional calculations were completed using the Gaussian03 and Gaussian09 suites of quantum mechanical programs [26,27].

3. Results and discussion

3.1. Formation of M(I) complexes by ion/ion reactions

The solutions of the metal salts and phenanthroline generally favor production of doubly-charged ions during ESI with two phenanthrolines bound to the M(II) metal center, M(II)Phen$_2^{+2}$ (throughout the manuscript, we will show the structures with neutral phenanthrolines – it is possible that in some species, charge transfer to the phenanthroline could occur to some extent). It is possible to prepare the mono-phenanthroline complexes, M(II)Phen^{+2}, by subjecting the bis-phenanthroline complexes to collision-induced dissociation (CID). The added steps in producing these ions led to somewhat lower signal intensities. Once isolated, the metal phenanthroline dication complexes can be subjected to ion/ion reactions with the fluoranthene radical anion using the ETD feature of the Thermo LTQ mass spectrometer. In typical experiments, an ion/ion reaction time of 200 ms was used to complete the reduction of the metal (the subsequent ion/molecule reaction times were 1000–9999 ms). In Fig. 1, spectra are given for the entire reaction sequence for the cobalt bis-phenanthroline system. Using this approach, it was possible to generate M(I)Phen^{+1} and M(I)Phen$_2^{+1}$ ions for iron, cobalt, nickel, copper, and zinc from their dication precursors. It appears that the M(I) species are very reactive with molecular oxygen and reactions with adventitious oxygen in the ion trap lead to addition products. The vacuum system of LTQ does not allow us to eliminate the background oxygen, but it is possible to study bimolecular chemistry despite the unwanted side reactions. Finally, it should be noted that in some cases, signals for M(I) species were observed in the ESI spectra of the starting solutions – reductions of this type during ESI have been observed previously [28]. These complexes produce the same products as the ETD-produced complexes.

3.2. Ion/molecule reactions of M(I) complexes

In our design, the neutral reagent enters the ion trap as part of the helium buffer gas and is held at a constant pressure throughout each stage of the experiment. An advantage of this approach is that the neutral gas reaches an equilibrium pressure and it is possible to conduct accurate kinetic measurements. A possible disadvantage is that the neutral reagent can react with precursor ions, including the fluoranthene radical anion. However, it has been proven that this interaction does not occur. As a result, the pressure of the neutral reagent must be carefully controlled so that the ion/ion reaction of the precursor dication is much faster than the reactions of the neutral reagent with the dication or with the fluoranthene radi-