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Ion–Molecule Reaction Chemistry of Fe$^+$ with NO: Excited- versus Ground-State Reactions

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Abstract: Ion–molecule reactions of excited- and ground-state Fe$^+$ with NO are reported. The charge-exchange and clustering ion–molecule reactions of Fe$^+$ with Fe(CO)$_5$ are used to study the reaction dynamics of metastable versus ground electronic state Fe$^+$ ions. The ground-state ^{6}D(4s^{1}3d^6) Fe$^+$ ions are unreactive with NO. Conversely, the metastable electronic states react with NO to form charge-transfer product ions (NO$^+$) and radiative association adduct ions [Fe$^+$(NO)] and by the collisional relaxation process. The collisional relaxation process gives rise to the ground-state ^{6}D(4s^{1}3d^6) and excited-state ^{6}S(4s^{2}3d^5) Fe$^+$ ions. The ^{6}S(4s^{2}3d^5) Fe$^+$ ion is unreactive with NO and constitutes approximately 6% of the Fe$^+$ ion population. Molecular orbital concepts are used to explain the lack of reactivity for the ^{6}S(4s^{2}3d^5) Fe$^+$ ions and also the collisional relaxation process by the high-lying 4s^{1}3d^6 states to form the ^{6}S(4s^{2}3d^5) Fe$^+$ ions.

Introduction

The gas-phase ion–molecule reaction chemistry of metal ions has been an active research area since the early 1970s.[1] In recent years an entirely new area of gas-phase inorganic and organometallic chemistry has emerged.[2] Prior to studies reported by Ridge and co-workers,[2g,h] it was generally assumed that the metal ions formed by dissociative ionization of gas-phase transition metal carbonyls were formed as ground-state ions or that any excited-state species formed decayed to ground-state ions at a rate that exceeded the bimolecular collision rate. Over the past several years detailed studies by several research groups have clearly established that excited states of metal ions are formed upon ionization of precursor molecules, especially by electron impact (EI) of metal carbonyl compounds, and that these metal ion excited states are long-lived (milliseconds to seconds). For example, Reents *et al.* observed that Cr$^+$ formed by dissociative ionization of Cr(CO)$_6$ reacted with CH$_4$ at two distinctive rates.[2g] Previous studies had shown that Cr$^+$ reacted exothermically with CH$_4$ only when Cr$^+$ is formed by electron impact.[3] Cr$^+$ ions formed by multiphoton ionization of Cr(CO)$_6$ appear to be formed entirely as ground-state species.[4]

Recent studies by a number of research groups have focused on comparing gas-phase ion–molecule reaction chemistry of ground and excited metal ion states. For example, Armentrout has used reaction cross sections to compare the reactivity of atomic transition metal ions (M$^+$) formed by surface ionization (SI) (yields predominantly ground-state population) and electron impact ionization (EI) (yields ground-state and excited-state population).[5] By making these comparisons, Armentrout and co-workers were able to measure the reaction chemistry of ground versus excited M$^+$ states. Kemper and Bowers have developed an electronic state chromatography (ESC) method that can be used to separate M$^+$ ions which have different electronic configurations (*e.g* d^n versus d^{n-1}s^1 configurations), and ESC can be used to study reactions of particular electronic configuration.[6] For instance, van Koppen and Bowers have recently used the ESC method to study the reactivity of ground and excited states of Co$^+$ and Fe$^+$ with propane[7] and have shown that the state-selected reactions of Co$^+$ and Fe$^+$ with propane are strongly dependent upon the electronic configuration of the reactant M$^+$ ion. For instance, the 3d^n states of Co$^+$ and Fe$^+$ react with propane more efficiently than the 4s^{1}3d^{n-1} states to form the collisionally stabilized M$^+$(C$_3$H$_8$) adduct ion. The ^{6}D(4s^{1}3d^6) Fe$^+$ ion also reacts with C$_3$H$_8$ to predominantly form the collisionally stabilized Fe$^+$(C$_3$H$_8$) adduct ion. The relative clustering efficiency of the ^{6}D(4s^{1}3d^6) Fe$^+$ ion is attributed to crossing of the ^{6}D(4s^{1}3d^6) Fe$^+$ ion to adiabatically react on the ^{4}F(3d^7) surface. The reduced clustering reactions of the 4s^{1}3d^{n-1} states are due to the repulsive occupancy of the 4s orbital. Tonkyn and Weisshaar have also compared the reactivity of 3d^n and 4s^{1}3d^{n-1} states of M$^+$ (M = Sc through Zn) ions formed by laser vaporization of solid metal targets with C$_2$H$_6$.[8] Their studies showed that M$^+$ ions with ground-state or low-energy d^n electron configurations react more efficiently to form the collisionally stabilized M$^+$(C$_2$H$_6$) adduct ion. The high reactivity of the 3d^n configuration *vis-à-vis* the 4s^{1}3d^{n-1} configuration can be rationalized on the basis of molecular orbital concepts. That is, the 3d^n electron configuration gives rise to a stronger interaction with C$_2$H$_6$, whereas the occupancy of the M$^+$ 4s orbital leads to a repulsive interaction.[8] Weisshaar and co-workers have also developed a resonance-enhanced multiphoton ionization angle-resolved time-of-flight photoelectron spectrometry method to generate specific electronic states of metal ions, and he has used this method to examine product ions formed by specific states.[9]

Although significant progress has been made in studies of state-selected ion–molecule reaction chemistry of metal ions, it is still difficult to accurately determine relative abundances of excited versus ground-state ions formed by various ionization methods.

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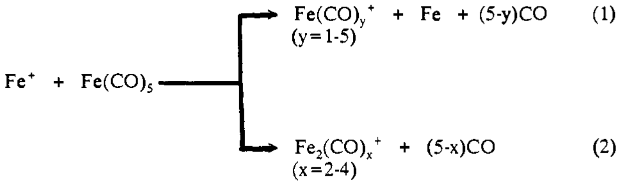
Also, it is difficult to estimate the range of energies of excited-state ions formed. The ESC method provides an accurate measurement of the relative abundance of various electronic configurations, and under surface ionization conditions, state-specific rate constants are readily obtained. However, this method does not always directly provide an estimate of the relative abundances of the metal ion excited states when highly excited states are present (*e.g.*, under electron impact conditions). To determine the relative abundance of metal ion excited states, we have recently developed a new technique using charge-exchange and clustering ion–molecule reactions. For example, Fe^+ formed by 70–25-eV electron impact ionization of $Fe(CO)_5$ reacts with neutral $Fe(CO)_5$ according to reactions 1 and 2.[10] Reactions



$$Fe^+ + Fe(CO)_5 \longrightarrow Fe(CO)_y^+ + Fe + (5-y)CO \quad (y=1\text{-}5) \qquad (1)$$

$$Fe^+ + Fe(CO)_5 \longrightarrow Fe_2(CO)_x^+ + (5-x)CO \quad (x=2\text{-}4) \qquad (2)$$

such as (1) may involve nondissociative and dissociative charge transfer, and reactions such as (2) yield ionic cluster fragments. The charge-transfer product ions (reaction 1) and ionic cluster fragments, $Fe_2(CO)_2^+$ and $Fe_2(CO)_3^+$, are formed by reactions of electronically excited states of Fe^+, whereas the $Fe_2(CO)_4^+$ ionic cluster fragment is formed by reaction of ground-state [$^6D(4s^13d^6)$] Fe^+ ions. We also reported the use of charge-exchange ion–molecule reactions for measuring relative abundances of metastable electronic states of metal ions.[10]

We are now using the charge-transfer ion–molecule reaction chemistry combined with two-section ion cell Fourier transform ion cyclotron resonance (FTICR) mass spectrometry to study the dynamics of collisional relaxation of metastable electronic states of M^+. In this paper we report the ion–molecule reaction chemistry of Fe^+ with nitric oxide. The ground-state $^6D(4s^13d^6)$ Fe^+ ions are unreactive with NO. Conversely, the excited states of Fe^+ react with NO *via* charge-transfer, radiative association [to form $Fe^+(NO)$], and collisional relaxation pathways. In addition, we have observed an excited state of the Fe^+ ion that is unreactive with NO. Charge-exchange ion–molecule reaction chemistry of Fe^+ with $Fe(CO)_5$ is used to bracket the electronic energy level of the unreactive Fe^+ ions. Molecular orbital concepts are used to explain the lack of reactivity of this particular Fe^+ excited state as well as the collisional relaxation process.

Experimental Section

These studies were performed on a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer that has been described previously.[11] The instrument consists of a home-built differentially pumped two-section ICR cell and vacuum system, an Extrel FTMS 2001 computer/electronics system, and a 3-T (15-cm bore) superconducting Oxford magnet. The two-section cell consists of two 3.8 × 3.8 × 3.8 cm cells that share a common trap plate which serves as a conductance limit. The conductance limit has an aperture of 1-mm radius in the center. The conductance limit aperture allows ions to transfer between the two differentially pumped cell regions.[12]

Samples were introduced into the cell by variable leak valves (Varian Model No. 951-5100) and maintained at a static pressure of 2×10^{-7} Torr as measured by Granville Philip Series 270 gauge controller. All experiments reported in this paper were performed in the two-section ion cell mode. $Fe(CO)_5$ was introduced to region 1, and nitric oxide was introduced to region 2. The partial pressures (2×10^{-7} Torr) of the reagents were measured by the ionization gauge in each region. Typically, the reactant Fe^+ ions were produced by 70-eV electron impact ionization of $Fe(CO)_5$. In order to probe the effect of electronic excitation of the reactant Fe^+ ions on the product ion distribution, the ionizing beam energy was varied between 55 and 25 eV. In these studies the electron beam energy was calibrated against the ionization energy of argon [15.759 eV for $Ar^+(^2P_{3/2})$].[13] The electron beam emission current traversing the ion cell is approximately 200 nA. The electron beam was pulsed on for a duration of 5 ms, and the ion cell trapping voltage was maintained at 4 V (*ca.* 105 V/m). Kinetic studies were performed according to a method described previously.[14] Pressure readings for NO were corrected for ionization gauge sensitivity according to the method described by Bartmess *et al.*[15] The corrected pressure reading was then used to calculate the hard sphere number density. The rate constants reported in this paper have an estimated experimental error of ±25%.

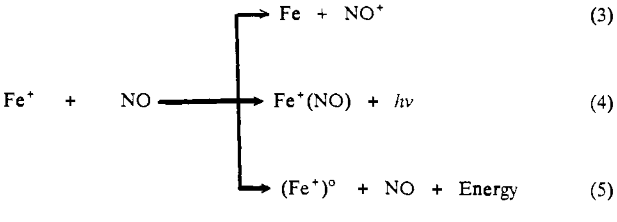
Fe^+ is initially formed by 70–25-eV electron impact ionization of $Fe(CO)_5$ in region 1 of the two-section cell. The reactant Fe^+ is then isolated by using ion-ejection techniques.[16] Ion ejection is accomplished by sweeping the rf oscillator over a range of frequencies ("chirp excitation" method). In these experiments, two ejection sweeps were used. The first ejection sweep was performed over a frequency range corresponding to m/z 18–36, and the second ejection sweep contained frequencies corresponding to m/z 76–300. The rf oscillator was swept over these two frequency ranges in order to eject all unwanted ions as well as to minimize translational excitation of Fe^+ ions caused by both "off-resonance" excitation and tailing of the chirp excitation.[17] Following the isolation step, Fe^+ is transferred to region 2 of the two-section ion cell and allowed to react with NO. The reaction time in region 2 was varied between 0 and 2 s.

Collisional relaxation studies of Fe^+ with NO were carried out as follows. Fe^+ is formed by 70–25-eV EI of $Fe(CO)_5$ in region 1 of the two-section ion cell. Fe^+ is then partitioned to region 2, where nitric oxide (or other collision gases) is maintained at a static pressure of 2×10^{-7} Torr. Fe^+ is allowed to react with NO (up to several seconds) before it is partitioned back to region 1 and allowed to react with $Fe(CO)_5$. The relative abundances of $Fe(CO)_y^+$ charge-transfer product ions are then used to estimate the energies and relative abundances of various excited states. In addition, the product ions of the charge-transfer reactions can be used to probe the relaxation dynamics of Fe^+ excited states. For example, the first excited state, $^4F(3d^7)$, reacts with $Fe(CO)_5$ to form $Fe(CO)_5^+$. The rate of collisional relaxation of the $^4F(3d^7)$ state can be determined by measuring the abundance of $Fe(CO)_5^+$ as a function of reaction time for Fe^+ with NO.

$Fe(CO)_5$ samples were obtained from commercially available sources (Strem Chemical Inc.). Nitric oxide was obtained from Matheson Gas Products, Inc. (MGP). Sample preparation involved freezing the $Fe(CO)_5$ sample in liquid nitrogen and pumping out air and other noncondensable gases for a period of a few minutes. Nitric oxide samples were used as received without further purification. It should be noted that the electron impact spectrum of the NO sample revealed three primary contaminants, *viz*, N_2, N_2O, and NO_2. The relative abundance of NO_2 appears to increase with time. That is, the amount of NO_2 impurity depends upon the time that the NO sample is exposed to light and an oxygen environment. To diminish NO_2 contamination, the NO transfer line was thoroughly evacuated and covered with aluminum foil prior to introducing the NO sample in the reaction chamber (ICR ion cell).

Results

This work investigates the gas-phase ion–molecule reaction chemistry of Fe^+ with NO. The primary objective of this work is to compare the reactivity of ground-state Fe^+ and metastable electronic states, denoted $(Fe^+)^*$, of Fe^+ with NO. We are particularly interested in the collisional relaxation of $(Fe^+)^*$ and in identifying reaction products that are unique to $(Fe^+)^*$. Fe^+ formed by 70–25-eV electron impact of $Fe(CO)_5$ reacts with NO to form two primary ionic products (reactions 3–5). Reactions 3 and 4 are exclusively due to reactions of $(Fe^+)^*$. Reaction 5



$$Fe^+ + NO \longrightarrow Fe + NO^+ \qquad (3)$$

$$Fe^+ + NO \longrightarrow Fe^+(NO) + h\nu \qquad (4)$$

$$Fe^+ + NO \longrightarrow (Fe^+)^\circ + NO + \text{Energy} \qquad (5)$$

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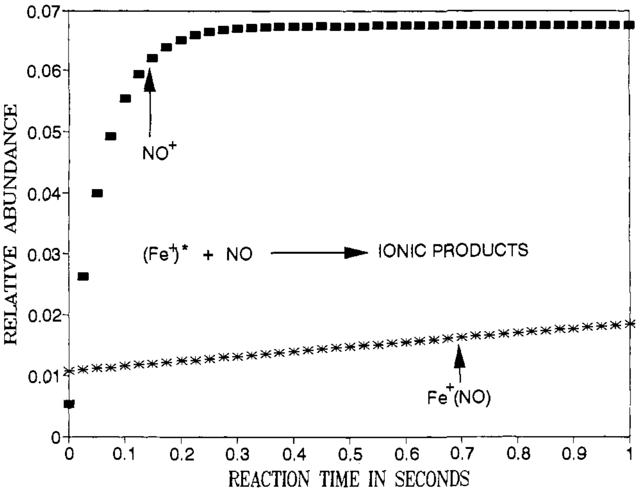

Figure 1. Plots of the normalized abundances of NO^+ and $Fe^+(NO)$ product ions as a function of the reaction time between Fe^+ and NO. The data used in these plots were treated according to the method described in ref 11. NO^+ (filled squares) and $Fe^+(NO)$ (asterisks).

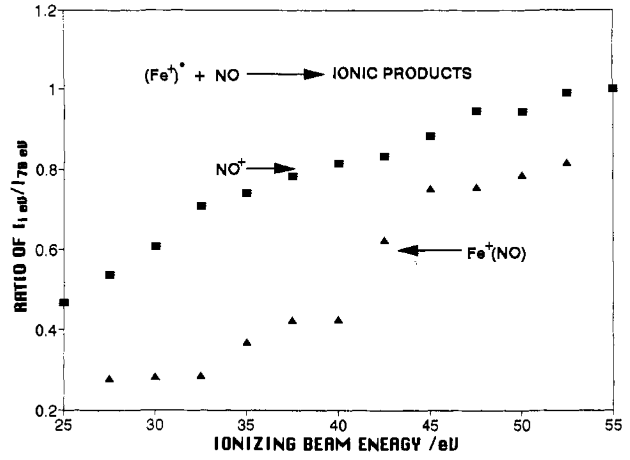

Figure 2. Plots of the ratio ($I_{i\,eV}/I_{70\,eV}$) of the three product ions of the reactions of Fe^+ with NO (reactions 3–5) as a function of the ionizing beam energy used to produce the reactant Fe^+. $I_{i\,eV}$ is the product ion abundance at *i* eV ionizing beam energy, whereas $I_{70\,eV}$ corresponds to product ion abundance at 70-eV ionizing beam energy. The reactant Fe^+ is formed by EI of $Fe(CO)_5$. No^+ (filled squares) and $Fe^+(NO)$ (filled triangles).

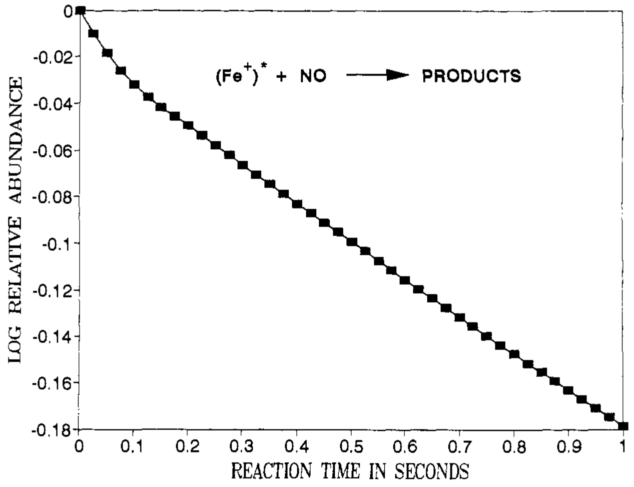

Figure 3. Plot of the logarithm of the relative abundance of Fe^+ ions as a function of reaction time with NO. The reactant Fe^+ is produced by 70-eV EI of $Fe(CO)_5$. The data plotted in Figure 4 were treated according to the method described in ref 11.

corresponds to the collisional relaxation process of the metastable electronic states of Fe^+. There are no detectable product ions attributed to the reactions of ground-state Fe^+ ions. It is possible that $Fe^+(NO)$ can also be a product ion formed by a reaction of Fe^+ with contaminant N_2O species. On the basis of studies (involving reactions of Fe^+ with N_2O) reported by Armentrout and co-workers,[18] and because the relative abundance of $Fe^+(NO)$ in our experiments is independent of the partial pressure of N_2O, we conclude that $Fe^+(NO)$ is formed by a reaction of $(Fe^+)^*$ with NO.

Figure 1 contains a plot of the normalized abundances of NO^+ and $Fe^+(NO)$ product ions as a function of reaction time between Fe^+ and NO. The curve corresponding to NO^+ (charge-transfer product ion) increases rapidly relative to the other product and then levels off at reaction times greater than 200 ms.

Figure 2 contains a plot of the ratio ($I_{i\,eV}/I_{70\,eV}$), where $I_{i\,eV}$ is product ion abundance at ionizing beam energy *i* eV and $I_{70\,eV}$ corresonds to product ion abundance at 70-eV ionizing beam energy, of the product ions of reactions 3–5 as a function of the ionizing beam energy used to produce the reactant Fe^+. The relative abundance of $Fe(NO)^+$ and NO^+ increases with increasing ionizing beam energy.

Figure 3 contains a plot of the logarithm of the relative abundance of the reactant Fe^+ ions as a function of the reaction time with NO. The semilogarithmic plot clearly shows two distinct slopes. That is, Fe^+ is initially depleted at a fast rate during the first 200 ms of reaction time, and the rate of depletion then decreases for reaction times greater than 200 ms.

Collisional relaxation of $(Fe^+)^* \rightarrow Fe^+$ was studied by forming Fe^+ by EI ionization of $Fe(CO)_5$ in region 1 of the two-section ion cell. Fe^+ is then partitioned to region 2, where the partial pressure of NO is maintained at 2×10^{-7} Torr. After reacting with NO for a specified period of time, Fe^+ is partitioned back to region 1 and allowed to react with $Fe(CO)_5$. Figure 4 contains a plot of the abundance of $Fe(CO)_y{}^+$ charge-transfer product ions as a function of the reaction time (residence time in region 2) between Fe^+ and NO. The abundance of $Fe(CO)_y{}^+$ (y = 1,3–5) decreases as the collisional relaxation time of the reactant Fe^+ is increased, indicating that the high-energy states of $(Fe^+)^*$ are depleted. Conversely, the abundance of the $Fe(CO)_2{}^+$ charge-transfer product ion remains constant even after 2 s of reaction time with NO, indicating that a high-lying excited state(s) of Fe^+ is unreactive with NO. The energy of the excited state(s) that is unreactive with NO must lie 2.86 ± 0.20 eV above the ground state; *e.g.*, the appearance energy of $Fe(CO)_2{}^+$ is 10.81 ± 0.2 eV[19] and the ionization energy of $Fe(CO)_5$ is 7.98 ± 0.01 eV.[20]

There has been some discussion about the composition of the *m/z* 56 signal formed by electron impact ionization of $Fe(CO)_5$. Bowers' research group observed a mass doublet at *m/z* 56 and suggested the possibility that the *m/z* 56 signal contains Fe^+ and possibly higher energy components that might undergo charge exchange with $Fe(CO)_5$, *e.g.*, $Fe(CO)_2{}^{2+}$, $(CO)_2{}^+$, etc.[21] We examined the *m/z* 56 signal by high mass resolution ($m/\Delta m$ = 12 000) (see Figure 5) and found only minor components, the most significant being $Fe(CO)_2{}^{2+}$. The abundance of the (Fe-

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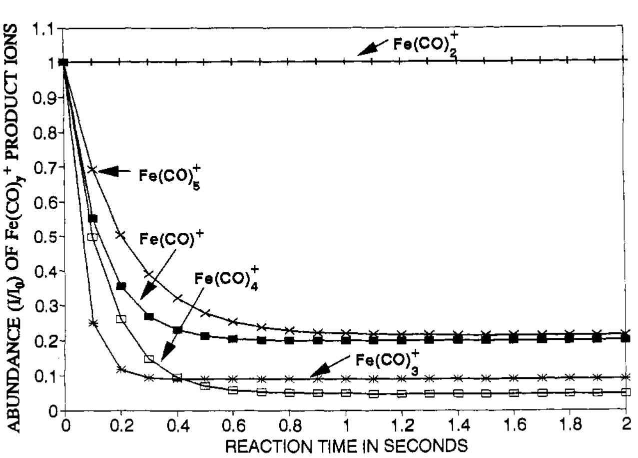

Figure 4. Plots of the relative abundance of Fe(CO)$_y$$^+$ charge-transfer product ions as a function of reaction time between the reactant Fe$^+$ [70–25-eV electron impact of Fe(CO)$_5$] and NO. The Fe(CO)$_y$$^+$ charge-transfer product ions are formed by reactions of Fe$^+$ with Fe(CO)$_5$.[10] Fe(CO)$^+$ (filled squares), Fe(CO)$_2$$^+$ (pluses), Fe(CO)$_3$$^+$ (asterisks), Fe(CO)$_4$$^+$ (empty squares), and Fe(CO)$_5$$^+$ (times signs).

(CO)$_2$)$^{2+}$ ion (less than *ca.* 2%) is too low to affect the results presented here or those we reported previously.[10]

Discussion

(Fe$^+$)* ions react with NO to form NO$^+$ (charge transfer) and Fe$^+$(NO) adduct ions with rate constants of 8 × 10^{-10} and 3 × 10^{-11} cm^3/s, respectively. The small rate constant (less than *ca.* 5% of the Langevin collision rate) for the formation of Fe$^+$(NO) and the low probability for third-body stabilizing collisions under the low-pressure (2 × 10^{-7} Torr) conditions of the experiment suggest that the initially formed collision complex, [(Fe$^+$)*---NO], is stablized by a radiative decay channel. It is interesting to note that the Fe$^+$(NO) ion is formed by a reaction of (Fe$^+$)* state(s) rather than reaction of ^{6}D(4s^{1}3d^6) Fe$^+$ ground-state ions. This observation further suggests that the [(Fe$^+$)*---NO] collision complex formed by (Fe$^+$)* ions has a decay channel that is not available to the [^{6}D(4s^{1}3d^6)Fe$^+$---NO]* collision complex. It is not clear from these experiments if the [^{6}D(4s^{1}3d^6)Fe$^+$---NO]* can be collisionally stabilized.

The use of charge-exchange ion–molecule reactions to measure the relative abundances of metastable electronic states of metal ions requires that certain fundamental assumptions be made. Of key importance is whether the excited metal ion states (M$^+$)* react to form the lowest energy product ions or react *via* channels that result in the lowest energy difference (ΔE) between the reactant (M$^+$)* states and the ionic products. In our previous paper[10] we examined this question and concluded that in the case of (Fe$^+$)* the preferred charge-transfer product ions are controlled by ΔE. Evidence supporting our conclusion comes from collisional relaxation studies of (Fe$^+$)* states which show that the high-lying (Fe$^+$)* states that give rise to the Fe(CO)$_2$$^+$ charge-transfer product ion are not depleted in reactions with NO. That is, the high-lying (Fe$^+$)* state(s) that are unreactive with NO react with Fe(CO)$_5$ to form exclusively Fe(CO)$_2$$^+$. Clearly, these (Fe$^+$)* states have sufficient energy to yield Fe(CO)$_y$$^+$ (y = 3–5) but react *via* a single reaction channel. Also, low ionizing energy (beam energies below *ca.* 35 eV) studies show preferential formation of high appearance energy Fe(CO)$_y$$^+$ product ions by high-lying (Fe$^+$)* states. For example, (Fe$^+$)* formed at near-threshold ionizing energy reacts with Fe(CO)$_5$ to form a greater amount of Fe(CO)$_y$$^+$ (y = 1–2) relative to Fe(CO)$_y$$^+$ (y = 3–4). These results suggest that (i) at low ionizing beam energy high-lying (Fe$^+$)* ions are formed in greater abundance than are the low-energy excited-state ions and (ii) the high-lying (Fe$^+$)* states react to form high-energy product ions, *e.g.*, y = 1–2. More detailed studies relating to conclusion i are currently underway.

Secondly, we carried out extensive studies measuring the relative abundances of metastable electronic states of (Fe$^+$)* involving other transition metal carbonyls.[21,22] These studies also included low ionizing beam energy as well as collisional relaxation studies. For example, Fe$^+$ was reacted with Cr(CO)$_6$ and the abundance of Cr(CO)$_y$$^+$ was used to bracket the energies of the (Fe$^+$)* ions. These results correlate very well (within experimental error) with the data obtained from reactions of (Fe$^+$)* with Fe(CO)$_5$. The relative abundances of the ground and excited states of Fe$^+$ determined by dissociative and nondissociative charge-transfer ion–molecule reactions are also in good agreement with those previously reported by Armentrout *et al.*, Bowers *et al.*, and Ridge *et al.*[22,23] We conclude from these studies that charge-transfer ion–molecule reactions provide a convenient experimental method for estimating the relative abundance of metastable electronic states. Again, we interpret these data in terms of the charge-transfer product ions accurately reflecting the energies of (Fe$^+$)* states. In particular, the high-lying (Fe$^+$)* states react to form Fe(CO)$_y$$^+$ rather than the lowest energy product ion Fe(CO)$_5$$^+$.

Another key question is whether Fe(CO)$_y$$^+$ product ions are formed by charge-transfer or ligand-exchange ion–molecule reactions. Armentrout and co-workers examined the reactions of translationally excited Fe$^+$ [^{6}D(4s^{1}3d^6)] with Fe(CO)$_5$ and concluded that the charge transfer and ionic cluster formation were the two main reaction channels.[24] To ensure that Fe(CO)$_y$$^+$ ions are indeed charge-transfer and not ligand-exchange product ions, reactions of ^{54}Fe$^+$ with Fe(CO)$_5$ were examined. ^{54}Fe$^+$ was isolated (see Experimental Section) from ^{56}Fe$^+$ and ^{57}Fe$^+$ isotopes following 70–25 eV electron impact ionization of Fe(CO)$_5$ and allowed to react with Fe(CO)$_5$ for 100 ms. Results from these studies show that ^{54}Fe$^+$ [70–25 eV EI of Fe(CO)$_5$] reacts with Fe(CO)$_5$ to produce ^{56}Fe(CO)$_y$$^+$ (y = 1–5) charge-transfer ionic products. ^{54}Fe$^+$ also reacts with Fe(CO)$_5$ to produce ^{54}Fe^{56}Fe(CO)$_y$$^+$ (y = 2–4) ionic cluster fragments. It is apparent from these results that Fe(CO)$_y$$^+$ are indeed charge-transfer product ions.

The accuracy of assigning electronic states by charge-exchange ion–molecule reactions depends upon the availability of accurate thermochemical data. In our earlier paper[10] we adopted appearance energy values reported by Distefano[20] because they seem to be the most widely accepted values. Ng and Armentrout subsequently reported appearance energies for Fe(CO)$_y$$^+$ (y = 0–5) that differ from the values reported by Distefano and adopted by Rosenstock.[25] For example, Ng and co-workers[26] report the appearance energy for Fe(CO)$_2$$^+$ as 10.84 ± 0.04 eV and 10.88 ± 0.05 eV on the basis of photoionization efficiency (PIE) and photoelectron–photoion coincidence (PEPICO) spectroscopic methods, respectively. On the basis of sequential bond energies of Fe(CO)$_y$$^+$ (y = 1–5) (determined by collision-induced dissociation measurements) Armentrout and co-workers[24] calculated an appearance energy value for Fe(CO)$_2$$^+$ as 10.85 ± 0.16 eV. The appearance energy obtained by Distefano on the basis of a photoionization method is 10.68 ± 0.1 eV.[20] The appearance energies that we will employ in this paper are the average of the values reported by Distefano, Armentrout, and Ng. That is, for the Fe(CO)$_2$$^+$ ionic fragment we adopt the average of the four appearance energy values, *viz.*, 10.81 ± 0.20 eV. The uncertainty in the average value was calculated by adding in quadrature. That is, the total error for the Fe(CO)$_2$$^+$ appearance energy was calculated by taking the square root of the sum of the squares

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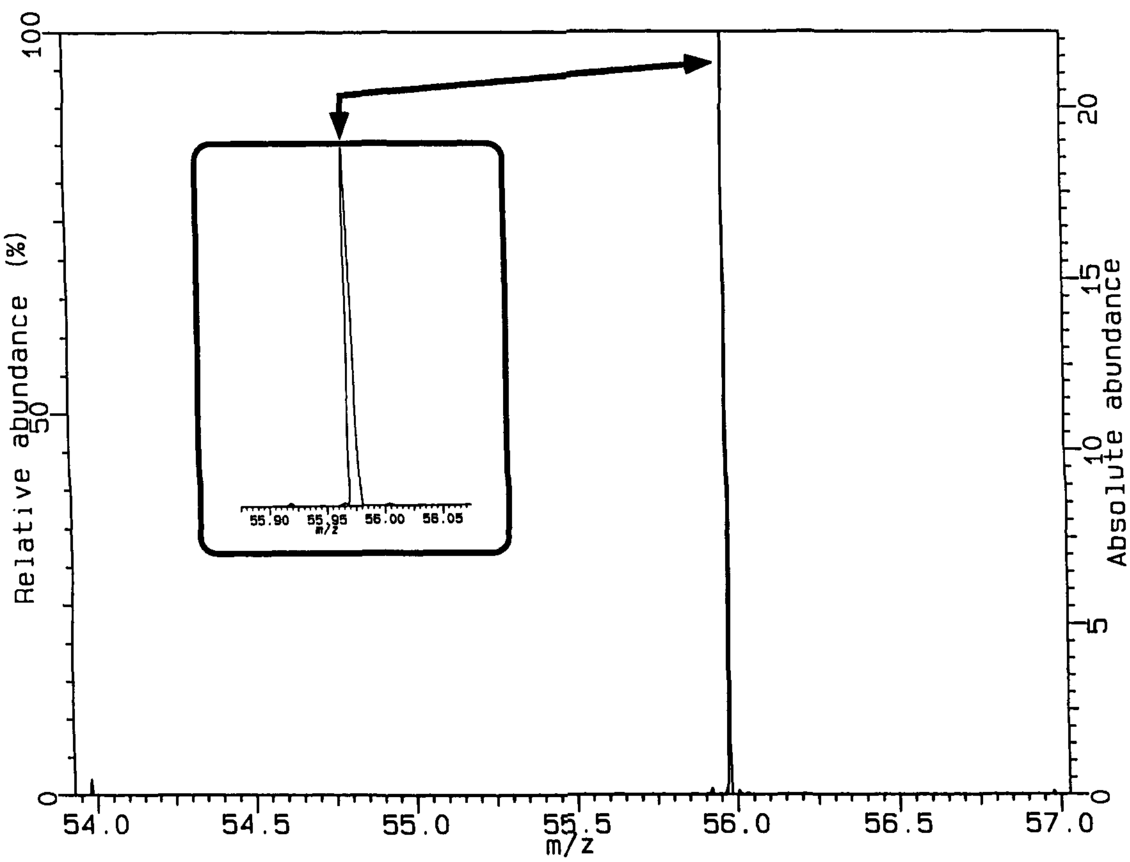

Figure 5. High mass resolution, $m/\Delta m$ = 12 000, spectrum of Fe^+ produced by EI of $Fe(CO)_5$. The insert shows the blown-up region of the m/z 56 signal. This spectrum clearly shows that the m/z 56 signal consists of the $^{56}Fe^+$ ion with less than *ca.* 2% contribution from higher energy components. The spectrum also shows $^{54}Fe^+$ and $^{57}Fe^+$ isotopes.

of the respective individual errors, $(\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2 + \epsilon_4^2)^{1/2}$. The average appearance energy determined in this manner is within the experimental error of all four literature values. It should be noted that the emphasis on the appearance energy of $Fe(CO)_2^+$ at this juncture is due to the fact that the $(Fe^+)^*$ state(s) which react to form this ion $[Fe(CO)_2^+]$ are not depleted in reactions with NO (this point is discussed in detail in the proceeding sections), and in this paper we are particularly interested in determining the energy of the nonreactive state(s).

The $Fe(CO)_2^+$ charge-transfer product ion is formed by reactions of a long-lived $(Fe^+)^*$ state(s) with an ionization energy greater than or equal to 10.81 ± 0.20 eV. The lowest lying of such states are the $^4F(4s^13d^6)$ and the $^6S(4s^23d^5)$ electronic states. The $^4F(4s^13d^6)$ (10.71 eV)[27] and the $^6S(4s^23d^5)$ (10.79 eV)[27] electronic states have approximately the same energy as the appearance energy of $Fe(CO)_2^+$. All other electronic states (with energies greater than 10.79 eV) with sufficient energies to form the $Fe(CO)_2^+$ charge-transfer product ion have the $4s^13d^6$ electron configuration.

The collisional relaxation of $(Fe^+)^*$ states with NO suggests that electronic states which react to form the $Fe(CO)_y^+$ (y = 1,3–5) charge-transfer product ions are reactive with NO, whereas $(Fe^+)^*$ state(s) that react to form $Fe(CO)_2^+$ ion are unreactive with NO. The data presented in Figure 1 suggest that $(Fe^+)^*$ states which charge-transfer with NO react very efficiently, *i.e.*, they react at a rate that approaches the Langevin collision rate. Although we do not know the specific electronic state(s) that react by reaction 3, on the basis of the ionization energy of NO (9.26 eV)[28] the $(Fe^+)^*$ ions must have energies greater than or equal to 1.31 eV above the energy of the $^6D(4s^13d^6)$ Fe^+ ion (7.95 eV + 1.31 eV = 9.26 eV). It is interesting to note that the $(Fe^+)^*$ ions which give rise to the $Fe(CO)_2^+$ charge-transfer product ion have sufficient energy to undergo charge-transfer reactions with NO but they appear to exhibit no such reactivity. Nonreactivity appears to be electron configuration specific.

Because $(Fe^+)^*$ states that react to form $Fe(CO)_y^+$ (y = 1,3–5) charge-transfer product ions are depleted in reactions with NO, it is apparent that the $4s^13d^6$ and $4s^03d^7$ electronic states react very efficiently with NO as well as other reagents (He, Ar, Kr, H_2, D_2, CO, N_2, CH_3OH, and CH_4).[29] The term "reactive" is used in this paper to include collisional relaxation reactions (such as reaction 5) as well as reactions that yield new ionic products. A plausible assignment for the unreactive $(Fe^+)^*$ is the $^6S(4s^23d^5)$ electronic state with an ionization energy of 10.79 eV.[30]

The lack of reactivity of the $^6S(4s^23d^5)$ Fe^+ ion with NO is rationalized using molecular orbital concepts adopted by Ridge,[2h] Armentrout,[31] and Weisshaar[8] to explain state-specific reactions of other metal ions (*e.g.*, first-row atomic transition metal ions) with various small organic molecules. For example, in the formation of the ion–molecule collision complex the 4s orbital of Fe^+ acts as the acceptor orbital and the singly occupied π^* orbital of NO acts as the donor orbital (Scheme I). Similarly, the unoccupied π^* orbital of NO acts as the acceptor orbital for the back-donation by the occupied 3d orbital of Fe^+. This type of synergistic interaction is known to occur in transition metal nitrosyl complexes. The key requirement in the back-bonding is that the Fe^+ d orbital(s) must be filled and of the correct symmetry to interact with the unoccupied π^* orbital of NO. Because the

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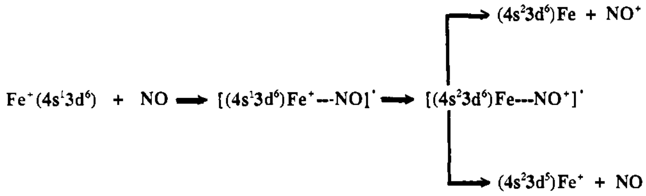
Scheme I



^{6}S(4s^{2}3d^5) Fe$^+$ ion has a fully occupied 4s orbital and stable half-filled d orbitals, bonding interactions between the ^{6}S(4s^{2}3d^5) Fe$^+$ and NO are weak and do not yield detectable product ions.

Scheme I suggests an interesting outcome for reactions of high-lying 4s^{1}3d^6 Fe$^+$ ions with NO. The 4s^{1}3d^6 Fe$^+$ states with energies greater than 10.71 eV react with NO according to Scheme I to form ^{6}S(4s^{2}3d^5) Fe$^+$ ion. For instance, reactions of 4s^{1}3d^6 Fe$^+$ states with NO result in the formation of a collision complex, and the s orbital of Fe$^+$ acts as the acceptor orbital for the single antiboding pπ (π^*) electron of NO. The overlap of the filled Fe$^+$ d orbital with the empty π^* orbital of NO results in back-donation of the Fe$^+$ d orbital electron into the NO π^* orbital. Subsequent dissociation results in the formation of ^{6}S(4s^{2}3d^5) Fe$^+$ ion. Conversely, donation of the single π^* orbital electron of NO into the s orbital of Fe$^+$ corresponds to charge transfer to form NO$^+$. On the basis of the data contained in Figure 4, the latter process does not appear to occur. That is, because the amount of the Fe(CO)$_2^+$ charge-transfer product ion does not change by a detectable amount, it is probable that the formation of ^{6}S(4s^{2}3d^5) Fe$^+$ ion by the decay of the high-lying states is the dominant process. The states with the 4s^{1}3d^6 electronic configuration that lie lower in energy than the ^{6}S(4s^{2}3d^5) state and have sufficient energy to undergo charge-transfer reactions with NO react primarily *via* the charge-transfer channel (reaction 3) whereas the 3d^7 states that have sufficient energy to undergo charge transfer but lie lower in energy than the ^{6}S(4s^{2}3d^5) state can undergo collisional relaxation and/or a charge-transfer process. The first excited state, ^{4}F(3d^7) Fe$^+$, and the second excited state, ^{4}D(4s^{1}3d^6) Fe$^+$, do not have sufficient energy to undergo charge-transfer reactions with NO. Collisional relaxation is probably the primary mode of reaction of the ^{4}F(3d^7) and ^{4}D(4s^{1}3d^6) states. The mechanism involved in the relaxation of the ^{4}F(3d^7) and ^{4}D(4s^{1}3d^6) states is not yet understood, but we clearly know that these two states do not have enough energy to charge transfer with NO. Therefore, a mechanism similar to Scheme I that requires charge transfer (NO + e$^-$ $\rightarrow$ Fe$^+$) within the [(Fe$^+$)*---NO] collision complex is not involved. Alternatively, the single π^* electron of NO can form a covalent bond with the lone 4s electron of the ^{4}D(4s^{1}3d^6) Fe$^+$ ion. ^{4}D(4s^{1}3d^6) Fe$^+$ $\rightarrow$ ^{6}D(4s^{1}3d^6) Fe$^+$ collisional relaxation can occur *via* vibrational excitation of the NO molecule.

Another plausible mechanism for the formation of the ^{6}S(4s^{2}3d^5) state involves a curve-crossing process similar to that proposed by Armentrout and co-workers[2b] to explain collisional relaxation of atomic transition metal ions (M$^+$) by noble gases. That is, the reactions of high-lying 4s^{1}3d^6 states can involve curve crossing between the 4s^{1}3d^6 and 4s^{2}3d^5 states followed by surface hopping to form the ^{6}S(4s^{2}3d^5) Fe$^+$ ion. Because the other collisional relaxation reagents do not show effects similar to that observed for NO in reactions with these states, it is likely that the curve crossing proposed by Armentrout is not applicable to the NO system. Because it is difficult to design experiments that unambiguously identify the mechanism of collisional relaxation, we have initiated theoretical studies that hopefully will delineate this issue.

Conclusion

Charge-exchange ion–molecule reactions can be used to measure the relative abundance of metastable electronic states of Fe$^+$ ions. This method can also be used to study the reaction dynamics of ground and excited states of Fe$^+$ ions. The results from these studies show that the metastable electronic states that have the 4s^{1}3d^6 configuration and lie higher in energy than the ^{6}S(4s^{2}3d^5) state react synergistically with NO to form the ^{6}S(4s^{2}3d^5) Fe$^+$ ions. The ^{6}S(4s^{2}3d^5) Fe$^+$ ion is unreactive with NO, even though this ion has sufficient energy to charge-transfer with NO. The results from these studies also show that the other (Fe$^+$)* ions react with NO to form NO$^+$ charge-transfer product ion and Fe$^+$(NO) radiative association adduct ion and by collisional relaxation to form the ^{6}D(4s^{1}3d^6) Fe$^+$ ion. The radiative association reaction pathway is very inefficient; *i.e.*, less than 5% of the collisions are reactive.

The collisional relaxation process is very efficient relative to the Langevin collision rate. On the basis of these studies the collisional relaxation process appears to involve more than one mechanism. For example, we see collisional relaxation to form two primary Fe$^+$ ions, *viz.*, the ^{6}D(4s^{1}3d^6) Fe$^+$ and ^{6}S(4s^{2}3d^5) Fe$^+$ ions.

Finally, reactions of Fe$^+$ with NO can be used to generate a population of Fe$^+$ ions that contains only the ground state ^{6}D(4s^{1}3d^6) and the ^{6}S(4s^{2}3d^5) excited state. When Fe$^+$ is generated by 70-eV EI of Fe(CO)$_5$ and allowed to react with NO, it is estimated that 94% of the ions consists of the ^{6}D(4s^{1}3d^6) ground-state and 6% as the ^{6}S(4s$_2$3d^5) excited-state ions. The population of these two Fe$^+$ ions was calculated using dissociative charge-transfer and clustering ion–molecule reaction chemistry. The chemistry of the ^{6}S(4s^{2}3d^5) state can be obtained by comparison with the known reaction chemistry of the ground-state ions.

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