

Reaction of FeC_5H_5^+ Ion with Neutral Ferrocene: The Dependence of Reaction Pathways on Its Internal Energy

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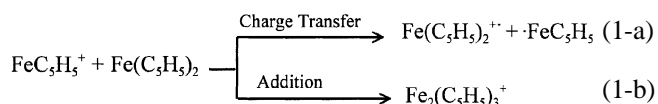
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The reaction of FeC_5H_5^+ ion with ferrocene molecule is investigated using FT-ICR mass spectrometry. FeC_5H_5^+ ions are generated by dissociative ionization of ferrocenes using an electron beam. The reaction gives rise to the formation of the adduct ion, $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$, in competition with charge transfer reaction leading to the formation of ferrocene molecular ion, $\text{Fe}(\text{C}_5\text{H}_5)_2^+$. The branching ratio of the adduct ion increases as the internal energy of the reactant ion decreases and correspondingly the branching ratio for the charge transfer reaction product decreases. The observed rate of the addition reaction channel is slower than that of the charge transfer reaction. The observation of the stable adduct ions in the low-pressure ICR cell is attributed to the radiative cooling of the activated ion-molecule complex. The mechanism of the reaction is presented to account for the observed experimental results.

Introduction

The reaction of the FeC_5H_5^+ ion with the neutral ferrocene has attracted much interest in recent years for the elucidation of the mechanism of the $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ cluster formation.¹⁻⁵ The formation of $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ was first reported by Muller *et al.* from their mass spectrometric study.¹ The kinetics of the $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ formation reaction was studied by Schildcrout using a double focusing mass spectrometer,² demonstrating that the reaction of FeC_5H_5^+ with ferrocenes leads an addition reaction forming the stable adduct ion in competition with a charge transfer reaction producing ferrocene molecular ion, $\text{Fe}(\text{C}_5\text{H}_5)_2^+$. Foster *et al.* reported their ion cyclotron (ICR) mass spectrometric studies³ and confirmed the reaction mechanism suggested by Schildcrout. These studies provided a two-channel picture as following.



Recently, Innorta *et al.* reported from their ion trap mass spectrometric studies that the branching ratio of the addition reaction channel increases as the background helium pressure increases at the range of 5×10^{-6} to 5×10^{-4} Torr.^{4,5} It was proposed that both channels go through a common activated reaction intermediate, $\text{Fe}_2(\text{C}_5\text{H}_5)_3^{*+}$, which dissociates to form the charge transfer reaction product or stabilizes to the adduct ion by collisional quenching with helium molecules. However, it is not clearly stated whether the dependence of the branching ratio on the helium pressure is due to the collisional quenching of $\text{Fe}_2(\text{C}_5\text{H}_5)_3^{*+}$ or the collisional cooling of the reactant ion itself. The collision rate constant of a gas phase ion is typically in the order of $1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ according to the ion-molecule collision theory.⁶ Thus, the collision interval of the inter-

mediate ion is expected to be 5 ms to 50 ms at the helium pressure of 5×10^{-6} to 5×10^{-4} Torr applied in the ion trap study. As most of activated ion-molecule reaction intermediates are known to have lifetime of ms time scale,⁸⁻¹¹ the collisional quenching is not expected to be a dominant reaction channel of $\text{Fe}_2(\text{C}_5\text{H}_5)_3^{*+}$ compared to other possible channels such as the unimolecular dissociation either backward to the reactants or forward to the charge transfer products. To establish the mechanism of the $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ cluster formation, the reaction kinetics are to be studied under well characterized collision environment.

The ionization potential of ferrocene is well known to be 6.75 eV from photoionization studies.¹² The ionization potential of iron cyclopentadienyl radical, estimated from relatively reliable thermochemical data in literatures ranges between 6.2 eV and 6.8 eV [see reference 13 for details]. The thermochemical estimation gives little guidance in deciding whether the charge transfer reaction channel is endothermic or exothermic. The reaction of FeC_5H_5^+ with several organic molecules were studied by Ekeberg *et al.*¹⁴ and Gwathney *et al.*¹⁵ They proposed that electron impact ionization of ferrocene may generate FeC_5H_5^+ in the long-lived excited electronic state, but their experimental results were not conclusive to support the proposition.

In this paper, we report our investigation of the reaction of FeC_5H_5^+ with neutral ferrocene using a Fourier transform ion cyclotron (FT-ICR) mass spectrometer. The FeC_5H_5^+ ions were generated by electron impact ionization of ferrocenes. The reaction rate for each channel is measured by monitoring the intensities of the reactant ion and the product ions as functions of reaction time. To investigate effects of the internal energy of the reactant ion, the branching ratios of the two channels are measured in the electron energy range of 10-50 eV. A reaction mechanism is proposed to account for our experimental results.

Experimental Section

All experiments were performed with a Finnigan FTMS-2000 Fourier transform-ion cyclotron mass spectrometer equipped with a 3.0 Tesla superconducting magnet and a differentially pumped dual cell. The dual cell consists of two 5.04 cm cubic assemblies serially aligned along the axial axis of the magnet field. In this work, ion formation and detection were achieved at the source side of the dual cell. The pressure in the ICR cell was measured with an ion gauge shielded with a magnetic field isolation box. The background pressure of the ICR cell is typically below 5×10^{-9} Torr. Ferrocene vapor was introduced to the source side of the cell with a reservoir inlet system. The sample pressure measured with the ion gauge was typically $\sim 2 \times 10^{-8}$ Torr. As measuring absolute rate constants is out of the scope of this study, calibration of the ion gauge was not performed. FeC_5H_5^+ ions were generated by electron impact ionization of ferrocenes. Double resonance ion ejection techniques were used to isolate FeC_5H_5^+ ions. For time-resolved detection of ion-molecule reactions, mass spectrum of ions inside the ICR cell was monitored as a function of delay time between isolation of the reactant ion and a broad band rf detection pulse. The branching ratios of the reaction products were measured by taking mass spectrum at 10 s after isolation of the reactant ions in the electron energy range 10–50 eV. The completion of the reaction was ensured from the time-resolved detection study. Ferrocene was obtained from Aldrich and used without further purification.

Results

The mass spectra obtained at 10 second after isolation of FeC_5H_5^+ (m/z 121) ions show that the major products of the reactions of the ions with neutral ferrocenes are the charge transfer reaction products, $\text{Fe}(\text{C}_5\text{H}_5)_2^{2+}$, at m/z 186 and the adduct ions, $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$, at m/z 307. After long time delay, at least 10 s in the experimental condition, the reactant ions disappear completely. $\text{Fe}(\text{C}_5\text{H}_5)_2^{2+}$ and $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ do not have further reactions in the experimental condition. These observations agree with the previous results reported by Innorta *et al.*^{4,5} and Foster *et al.*³

We investigated the effect of the internal energy of the reactant ion, FeC_5H_5^+ , on the product branching ratio. A few methods were employed to adjust the internal energy. The branching ratios of the two channels measured as functions of the ionization electron energy are shown in Figure 1. The branching ratio for the charge transfer reaction shows a gradual increase as the electron energy increases while the ratio for the addition reaction channel decreases: 65% of $\text{Fe}(\text{C}_5\text{H}_5)_2^{2+}$ and 35% of $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ at 10 eV; 94% and 6%, respectively, at 50 eV. The branching ratios showed little change upon the introduction of helium gas up to 5×10^{-7} Torr measured by the ion gauge. It was impossible to observe a mass spectrum at further higher helium pressure due to a significant collisional damping of the detected ICR signal. At moderate helium pressure of 7×10^{-8} Torr, a weak

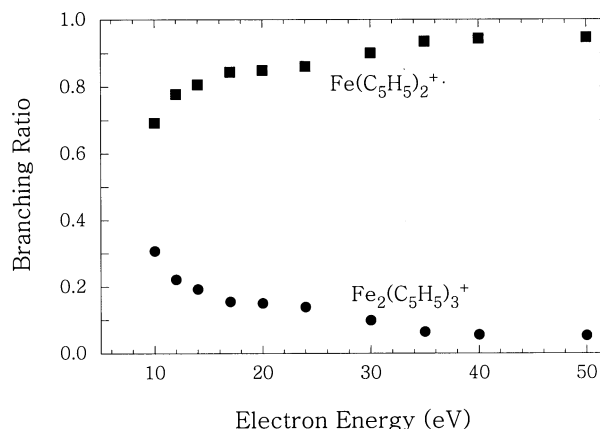


Figure 1. The branching ratios of the charge transfer reaction and the addition reaction of FeC_5H_5^+ ion with neutral ferrocene as functions of the ionization electron energy

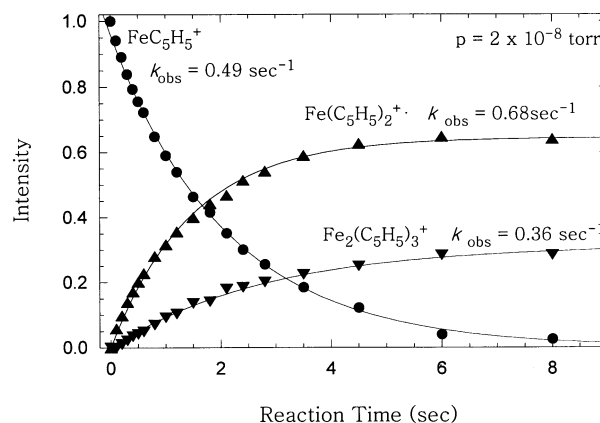


Figure 2. Time-resolved reaction spectrum for the reaction of FeC_5H_5^+ with neutral ferrocene. The ionization electron energy was 12 eV. The solid curves are obtained by fitting the time-resolved spectrum to the pseudo-first-order rate equation.

resonant rf pulse was applied to the FeC_5H_5^+ ions to induce collisional excitation of the ions,^{16,17} and the branching ratio of $\text{Fe}(\text{C}_5\text{H}_5)_2^{2+}$ ions noticeably increased. These results indicate that FeC_5H_5^+ ions with higher internal energy produce more $\text{Fe}(\text{C}_5\text{H}_5)_2^{2+}$ ions than the ions with lower energy.

Time-resolved reaction spectrum of FeC_5H_5^+ ions in the presence of ferrocene molecules is shown in Figure 2. No buffer gas was introduced into the ICR cell during the observation. The intensities of $\text{Fe}(\text{C}_5\text{H}_5)_2^{2+}$ and $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ show exponential increases, but the $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ ion shows a slower increase than the $\text{Fe}(\text{C}_5\text{H}_5)_2^{2+}$ ion. The rate of the formation of each product ion is obtained by fitting the time-resolved spectrum to the pseudo-first-order rate equation. The observed rate of the formation of $\text{Fe}(\text{C}_5\text{H}_5)_2^{2+}$ is $0.68 \pm 0.02 \text{ s}^{-1}$, while that of $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ formation is $0.36 \pm 0.02 \text{ s}^{-1}$. As it is not clear in the spectrum whether the decay signal of the reactant ion is bi-exponential, the signal is fitted to a single exponential decay equation. The observed rate of $0.49 \pm 0.01 \text{ s}^{-1}$ is near the average of the formations of the two products. The numbers given after “ \pm ” are the uncertainties coming from fitting the time resolved reaction

spectrum.

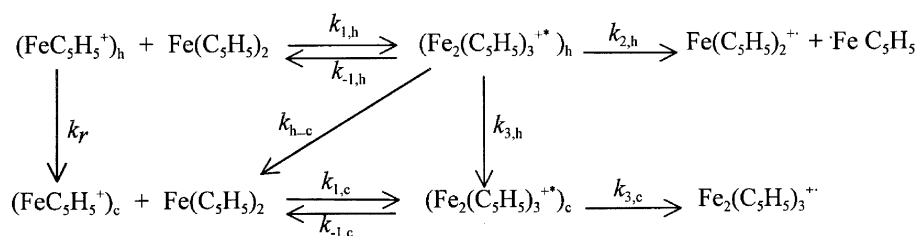
Discussion

It is interesting to observe the formation of the stable adduct ion, $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$, in the low pressure ICR cell without additional introduction of buffer gases. In gas phase, an effective cooling of the activated reaction intermediate, $\text{Fe}_2(\text{C}_5\text{H}_5)_3^{+*}$, is necessary for the intermediate to be stabilized as an adduct ion. Internally excited ions in gas phase are known to be stabilized by either collision with neutral molecules or radiative transition to low energy states.⁷⁻¹¹ At the ferrocene neutral pressure of 2×10^{-8} Torr, the collision rate of the intermediate ion-molecule complex, $k_c[\text{M}]$ where $[\text{M}]$ is the density of all the neutrals, is estimated to be approximately 0.5 sec^{-1} based on the the average dipole orientation theory.⁶ As this rate is too slow, the collisional cooling of the relatively short-lived activated intermediates to the stable adduct ions cannot compete with the unimolecular dissociation either toward the charge transfer reaction products or backward to the reactants.⁷⁻¹¹ Thus, the observation of the adduct ions in our experimental condition indicates that the formation of the adduct ions is due to the rapid radiative cooling of the activated intermediates, but not due to the collisional cooling. In contrast, Innora *et al.*^{4,5} proposed the collisional cooling of the intermediate as a major channel of the cooling processes to explain their ion trap mass spectrometric studies, in which they observed the increase of the branching ratio of $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ by increasing helium pressure at the range of 5×10^{-6} to 5×10^{-4} Torr. At even the highest helium pressure applied in the ion trap study, the collision interval of the intermediate is estimated to be approximately 50 ms, which is too long compared to the expected lifetime of the intermediate.⁷⁻¹¹ We note that the collisional cooling of the reactant ions by the buffer gas is more effective than that of the short-lived intermediates. Also, our experimental results show that decreasing the internal energy of the reactant ions increases the branching ratio of $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$. Correspondingly, the increase of the branching ratio of $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ by increasing helium pressure, observed by Innora *et al.*, could be at least partly due to the increased collisional cooling rate of the reactant ion itself.

It is remarkable to observe the difference between the rate of the two product channels and the internal energy dependence of their branching ratios. Though it is not unusual to observe the internal energy dependence of their branching

channel mechanism. According to the two-channel mechanism, the formations of the two products and the decay of the reactant ion must have the same reaction rate. It is unlikely that the two channels from the same reactants have different rates even in the case when the two channels have different reaction intermediates. If the two channels are through two different structural isomers of FeC_5H_5^+ , which may be generated from the dissociative ionization of ferrocenes, the two channels might have different reaction rates. However, the collisional cooling would not change the branching ratios because it is not expected to change the ratio of the isomers. Also, the FeC_5H_5^+ ion is structurally simple and is unlikely to have a structure other than the most stable structure with iron cation sitting on the cyclopentadienyl ring.¹⁸ We rather propose that the charge transfer reaction is either endothermic or has a slight activation barrier if it is exothermic. The presence of the activation barrier for an exothermic charge transfer reaction is expected if the ground electronic state of the reaction products (radical cation + radical, open shell) does not correlate to the ground electronic state of the reactant (closed shell) or the reaction intermediate (closed shell). In this case, the reaction goes through an avoided curve crossing, which causes considerable level of activation barrier for the reaction channel.¹⁹ In either case, the reactant ion must have internal energy higher than the reaction threshold to produce the charge transfer products. Our proposal of the presence of activation barrier in the charge transfer reaction well predicts the dependence of the product branching ratios on the internal energy of the reactant ion. According to the proposed mechanism, the FeC_5H_5^+ ions with internal energy lower than the charge transfer reaction threshold can produce only the adduct ions while the FeC_5H_5^+ ions with internal energy higher than the threshold can proceed into both channels. At lower ionization electron energy the internal energy distribution of the FeC_5H_5^+ ions shifts to the low energy side. Thus, the branching ratio of the addition reaction channel is expected to increase at the lower electron energy. The increase of the branching ratio of the charge transfer product upon applying a resonant rf pulse to FeC_5H_5^+ ions support the mechanism as the rf pulse induces the collisional excitation of the ions in the presence of buffer gases.

Considering the presumed presence of activation barrier for the charge transfer reaction and the difference of the reaction rate of the two channels, the following reaction mechanism is proposed.



ratios, the difference between the observed rate of the two product channels can not be explained by the simple two-

The mechanism divides the reactant ions, FeC_5H_5^+ , to two groups; $(\text{FeC}_5\text{H}_5^+)_h$ with internal energy higher than the

threshold of the charge transfer reaction channel, and $(\text{FeC}_5\text{H}_5^+)_c$ with internal energy lower than the threshold. The reaction intermediate, $(\text{Fe}_2(\text{C}_5\text{H}_5)_3^{+*})_h$, formed from $(\text{FeC}_5\text{H}_5^+)_h$ has excess energy to dissociate into the charge transfer product ($k_{2,h}$). This dissociation channel competes with the radiative cooling of the intermediate ($k_{3,h}$) and backward dissociation to the reactants ($k_{1,h}$ and $k_{h,c}$). It is well known that backward dissociations of ion-molecule complexes generate reactant ions with significantly lower internal energy than their original reactant ions due to the internal energy redistribution of the complexes.²⁰ Thus, the backward dissociation of $(\text{Fe}_2(\text{C}_5\text{H}_5)_3^{+*})_h$ is expected to generate mostly $(\text{FeC}_5\text{H}_5^+)_c$. The radiative cooling of $(\text{FeC}_5\text{H}_5^+)_h$, k_r , also generate $(\text{FeC}_5\text{H}_5^+)_c$. According to the proposed mechanism, the rate of the formation of $\text{Fe}(\text{C}_5\text{H}_5)_2^{+*}$ is the same with the decay rate of $(\text{FeC}_5\text{H}_5^+)_h$. $(\text{FeC}_5\text{H}_5^+)_c$ is continuously generated by the cooling of $(\text{FeC}_5\text{H}_5^+)_h$ through the backward dissociation ($k_{h,c}$) of intermediate $(\text{Fe}_2(\text{C}_5\text{H}_5)_3^{+*})_h$ or by the radiative cooling (k_r). Thus the decay of $(\text{FeC}_5\text{H}_5^+)_c$ must be slower than the decay of $(\text{FeC}_5\text{H}_5^+)_h$. Correspondingly, the formation of $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ is expected to be slower than the formation of $\text{Fe}(\text{C}_5\text{H}_5)_2^{+*}$. This mechanism predicts that the rate of the formation of $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ is slower than that of $\text{Fe}(\text{C}_5\text{H}_5)_2^{+*}$. Therefore, the proposed mechanism successfully predicts the observed kinetic results. The mathematical description of the time-profile of the intensity of each ion species is rather complicated and decided to set out of the scope of this report.

Under our experimental results, it is not clear whether the $(\text{FeC}_5\text{H}_5^+)_h$ can be attributed to ions in a long-lived excited electronic state or vibrationally excited ions in the ground electronic state. However, it is apparent that the energetics of the reaction channels is important for the interpretation of our experimental results. The proposed mechanism calls for the theoretical calculations of the energetics, the structures, and the electronic configurations of chemical species involved in the reaction and transition states along the reaction coordinate.

The formation of the presumed triple-decker sandwich adduct ion at low pressure does not seem to be confined to the iron compound. In a preliminary investigation on the reaction of NiC_5H_5^+ with $\text{Ni}(\text{C}_5\text{H}_5)_2$, we also observed the formation of the adduct ion, $\text{Ni}_2(\text{C}_5\text{H}_5)_3^+$, but the yield was very low compared to its iron analogue. Currently, the collisionally induced dissociation of isotope labeled $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ is under way to elucidate the structure of the adduct ion.

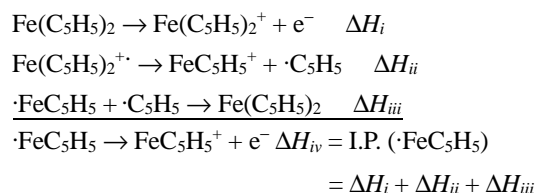
Conclusion

The gas phase ion chemistry of ferrocene was studied using FT-ICR mass spectrometry. The ion-molecule reaction of FeC_5H_5^+ with ferrocene in the low pressure ICR cell have two competing reaction channels; formation of the adduct ion, $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$, and charge transfer reaction leading to the formation of ferrocene molecular ion, $\text{Fe}(\text{C}_5\text{H}_5)_2^{+*}$. The branching ratio for the addition reaction increases as the internal energy of the reactant ion decreases and correspond-

ingly the ratio of the charge transfer reaction decreases. The observed rate of the addition reaction channel is slower than that of the charge transfer reaction. The observed results are considered to be due to the presence of the activation barrier for the charge transfer reaction. The mechanism of the reaction is proposed to account for the experimental results.

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- The ionization potential of iron cyclopentadienyl radical is derived from the following Hess' Law Calculation:



where, ΔH_i is the ionization potential of $\text{Fe}(\text{C}_5\text{H}_5)_2$, which is known to be 6.75 eV;¹² ΔH_{ii} is the bond dissociation energy of $\text{Fe}(\text{C}_5\text{H}_5)_2^{+*}$ to FeC_5H_5^+ and $\cdot\text{C}_5\text{H}_5$. $-\Delta H_{iii}$ is the the bond dissociation energy of $\text{Fe}(\text{C}_5\text{H}_5)_2$ to $\cdot\text{FeC}_5\text{H}_5$ and $\cdot\text{C}_5\text{H}_5$, which is known to be 3.94 ± 0.13 eV from a low pressure photolysis study on ferrocene.^{13a} However, ΔH_{ii} is a field of considerable discrepancies. The value obtained from a photoionization study is 6.41 ± 0.04 eV,^{13b} which is much higher than recently obtained data; 4.6 ± 0.4 eV from an electron impact study,^{13c} 3.7 ± 0.3 eV from a photodissociation study;^{13d} 3.95 eV from a photoionization study, which goes toward the upper limit of the photodissociation study.^{13e} We estimated I.P. ($\cdot\text{FeC}_5\text{H}_5$) using ΔH_{ii} from references 13d and 13e, which is considered to be relatively reliable compared to the older studies. The estimated value ranges between 6.2 eV and 6.8 eV.

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