by suction filtration followed by addition of 2 mL of 10% HCl to convert the hydrazine to its hydrochloride salt. The THF and water were evaporated and the residue dissolved in a minimum amount of CH_3CN. After addition of powered NaOH the solution was shaken for 15 min. The hydrazine was isolated from this mixture by preparative gas chromatography with use of a column temperature of 50 °C, an injector temperature of 100 °C, a detector temperature of 150 °C, and a He flow rate of 25 mL/min. Under these conditions the hydrazine had a 13 min retention time. ^2H NMR (CH_3CN) (internal $CDCl_3$ standard) δ 1.85 (s, 12 D).

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Kinetic and Photochemical Studies of $FeC_5H_6^+$ in the Gas Phase

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Abstract: Kinetic and photochemical studies were performed on $FeC_5H_6^+$. $FeC_5H_6^+$ was prepared by reacting Fe^+ with cyclopentene and subsequently with propane to give the cyclopentadienylallyliron ion. $D°(Fe^+\text{–cyclopentadiene})$ was determined by photodissociation threshold measurements to be 55 ± 5 kcal/mol, which in turn indicates that dehydrogenation of cyclopentene by Fe^+ is 33 ± 5 kcal/mol exothermic. Linear kinetics are observed by collisionally cooling the $FeC_5H_6^+$ ions in a high-background pressure of argon and yield a rate constant of $5 \pm 2 \times 10^{-10}$ cm³/(molecule·s), corresponding to a reaction efficiency of about 0.4. Photodissociation of the cyclopentadienylallyliron ion yields two product ions, $FeC_8H_8^+$ and $FeC_6H_6^+$, with the latter pathway, the higher energy process, prevailing when there is no background argon. The dehydrogenation pathway, the lower energy process, becomes more important when background argon is present to remove the excess energy from the parent ion. These results are in qualitative agreement with collision-induced dissociation experiments. Finally, $D°(CpFe^+\text{–}H) = 46 \pm 5$ kcal/mol is determined by photodissociation threshold measurements, which in turn yields $D°(Fe^+\text{–}Cp) = 88 \pm 7$ kcal/mol.

Introduction

Recently, we have begun investigating the effect of a series of ligands including alkanenitriles, arenes, and alkenes on the reactivity of gas-phase Fe^+ with propane.[1] These π-type ligands are observed not only to slow the reaction significantly but also in certain cases to open up new reaction channels. For example, at extended trapping times in a high-background pressure of propane, reactions 1–4 occur when L is an arene or alkene ligand and reactions 1–3 occur when L is an alkanenitrile ligand. In contrast, only reactions 2 and 3 are observed for bare Fe^+ with propane.[2] During the course of this study, cyclopentadiene was observed to have a unique effect on the reaction of Fe^+ with propane. Subsequently, an in-depth study was performed on this reaction system and the results are described here.

$$FeL^+ + C_3H_8 \rightarrow FeLC_3H_8^+ \quad (1)$$

$$\rightarrow FeLC_3H_6^+ + H_2 \quad (2)$$

$$\rightarrow FeLC_2H_4^+ + CH_4 \quad (3)$$

$$\rightarrow FeLC_2H_2^+ + CH_4 + H_2 \quad (4)$$

Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer previously described in detail.[3] The instrument is equipped with a 5.2 cm cubic trapping cell situated between the poles of a Varian 15 in. electromagnet maintained at 0.9 T. The cell utilizes two 80% transmittance stainless steel screens as the transmitting plates, permitting the irradiation of the interior with various light sources. Fe^+ was generated by focusing the beam of a Quanta Ray Nd:YAG laser (operated at 1.064 μm) onto a thin high-purity iron target. Details of the laser ionization experiment are described elsewhere.[4]

All chemicals were obtained in high purity from commercial sources and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensible gases. Sample pressures were measured with an uncalibrated Bayard-Alpert ionization gauge. For the kinetics experiment, the propane pressure was calibrated by using a rate constant of 1.1×10^{-9} cm³/(molecule·s) for reaction 5 and accounting for the different sensitivities of the ion gauge for propane and methane by using an experimentally determined factor of 1.8 from the literature.[5,6]

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \quad (5)$$

Details of the collision-induced dissociation (CID) experiment have been described previously.[7] The collision energy can be varied typically in the range 0–100 eV. The spread in kinetic energy depends on the average kinetic energy and is typically about 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.[8] CID product ion distributions are reproducible conservatively to ±15% absolute.

The details of the photodissociation experiment have been described elsewhere.[9] Ions to be studied by photodissociation were first isolated

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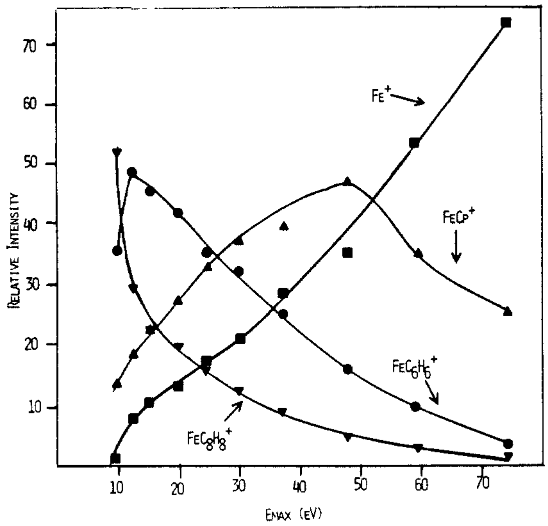
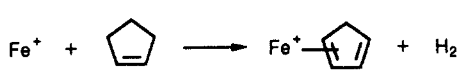


Figure 1. CID on $FeC_8H_{10}^+$ from the reaction of $FeC_5H_6^+$ with propane.

and then trapped in the cell for a period of a few seconds, during which time they were irradiated with light from a 2.5 kW Hg-Xe arc lamp used in conjunction with a Schoeffel 0.25 m monochromator. The threshold for a particular photodissociation reaction was determined by using a series of cutoff filters.

$FeC_5H_6^+$ was formed by the dehydrogenation reaction 6 of Fe^+ with cyclopentene, which was introduced into the vacuum chamber through a General Valve Corporation Series 9 pulsed solenoid valve.[10] The


(6)

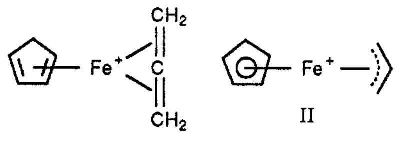
pulsed reagent gas fills the chamber to a maximum pressure of about 10^{-5} Torr with about a 150 ms rise time and is pumped away by a high-speed diffusion pump in about 250 ms. The cyclopentene pressure to the pulsed valve and the open-time of the valve were adjusted such that most of the Fe^+ reacted to give $FeC_5H_6^+$, and the secondary reaction to give ferrocene cation was suppressed.[11] The $FeC_5H_6^+$ ions were then isolated by swept double resonance ejection pulses and further experiments performed.

Results and Discussion

Reactivity of Fe⁺–Cyclopentadiene. $FeC_5H_6^+$ reacts rapidly with propane to give the double dehydrogenation product $FeC_8H_{10}^+$ exclusively, reaction 7, in contrast to reactions 1–4. Structures

$$FeC_5H_6^+ + C_3H_8 \rightarrow FeC_8H_{10}^+ + 2H_2 \qquad (7)$$

I and II may be postulated for the product ion. Reacting $FeC_5H_6^+$ with perdeuterated propane yields 92% $FeC_8H_5D_5^+$ and 4% each of $FeC_8H_6D_4^+$ and $FeC_8H_4D_6^+$, strongly supporting structure II over structure I. To further probe the structure of $FeC_8H_{10}^+$, its CID spectra at a series of kinetic energies were obtained, reactions 8–11 and Figure 1. Since the fragments $FeC_5H_6^+$ and $FeC_3H_4^+$


I II

$$FeC_8H_{10}^+ \xrightarrow{\text{CID}} FeC_8H_8^+ + H_2 \qquad (8)$$

$$\rightarrow FeC_6H_6^+ + C_2H_4 \qquad (9)$$

$$\rightarrow FeC_5H_5^+ + C_3H_5 \qquad (10)$$

$$\rightarrow Fe^+ + (C_8H_{10}) \qquad (11)$$

would be expected for structure I, particularly at higher collision energies, the CID results also favor structure II over structure I. Absence of an Fe^+–C_3H_5 fragment suggests that $D°(Fe^+–C_5H_5) > D°(Fe^+–C_3H_5)$. Formation of Fe^+ in reaction 11 may arise due to direct cleavage of intact C_8H_{10} or by sequential loss of two or more neutrals. Thus, C_8H_{10} appears in parenthesis in reaction 11.

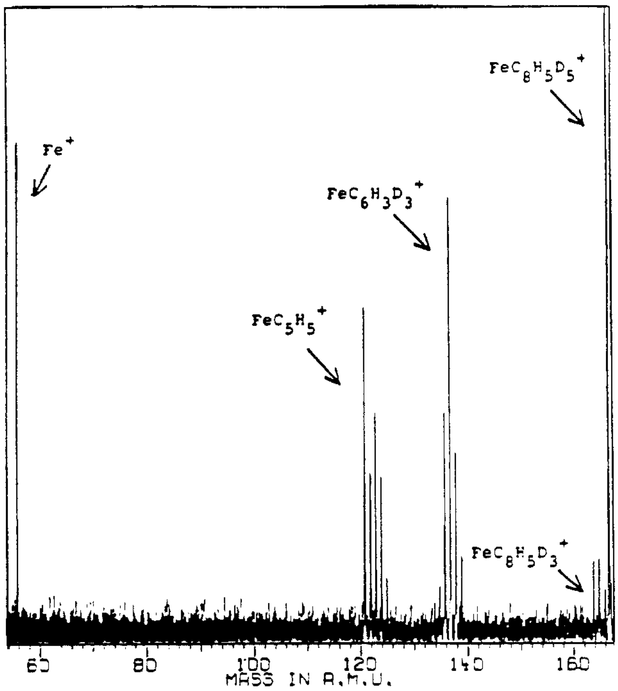
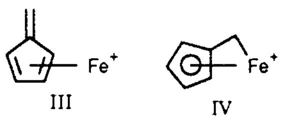


Figure 2. CID on $FeC_8H_5D_5^+$ at 47 eV.

It has been shown that Fe⁺–cyclopentadiene can easily rearrange to hydridocyclopentadienyliron ion.[11,12] One result supporting this rearrangement process is the reaction of $FeC_5H_6^+$ with benzene in which H• is displaced from the reactant ion to give FeCp⁺–benzene. It is probably through this rearrangement that the cyclopentadiene ligand plays an important role in reaction 7. During the reaction process, a hydrogen atom can migrate to the metal ion center from cyclopentadiene and be eliminated together with another hydrogen atom resulting from the oxidative insertion of the metal ion center into a propane C–H bond. The high stability expected for structure II provides the driving force for the reaction.

In hopes of obtaining information on the structures of the fragment ions from reactions 8–10 and, thus, acquiring more mechanistic information on the fragmentation, the product ion $FeC_8H_5D_5^+$ formed from C_3D_8 was subjected to CID. As shown in Figure 2, rather extensive H/D scrambling between the cyclopentadienyl ring and the deuterated allyl ligand is observed. CID of $FeC_6H_6^+$ formed in reaction 9 results in C_6H_6 loss, exclusively. When trapped in the presence of perdeuterated propene, C_3D_6, however, it undergoes two H/D exchanges. This result indicates two unique hydrogen atoms, ruling out Fe⁺–benzene as the structure and suggesting either Fe⁺–fulvene, structure III, or its resonance form η^6-(methylenecyclopentadienyl)iron ion, structure IV. Further support for either structure III or IV is obtained from the CID of $Fe(C_6H_6)(C_6D_6)^+$ formed from the condensation of perdeuterated benzene with $FeC_6H_6^+$ from reaction 9. CID at 22 eV yields $FeC_6H_4D_2^+$ and $FeC_6H_5D^+$ in comparable intensities. This indicates a scrambling process, re-


III IV

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(10) Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 57.

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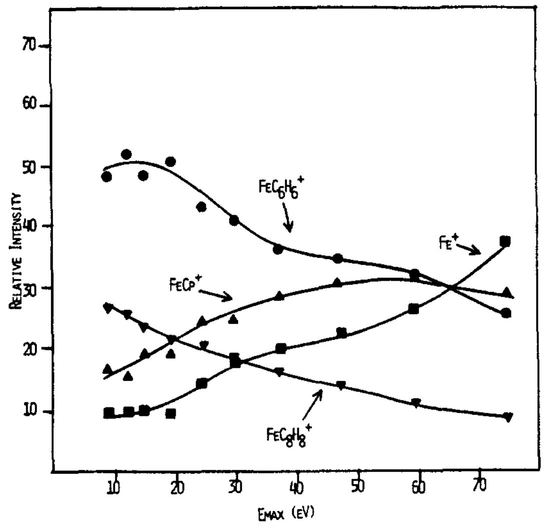
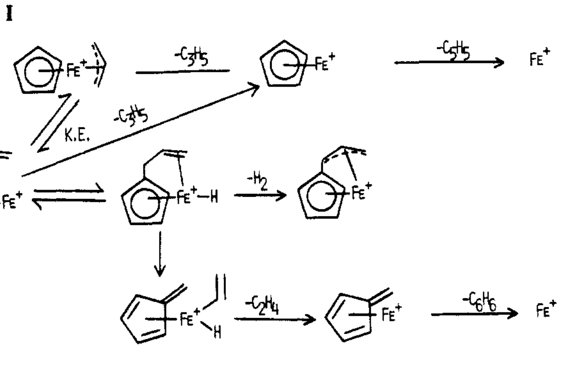
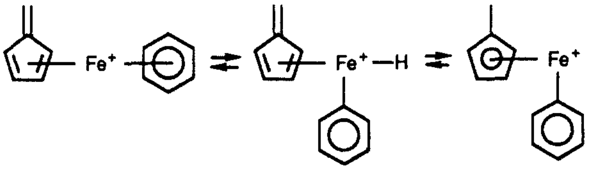


Figure 3. CID on $FeC_8H_{10}^+$ from the reaction of Fe^+ with allylcyclopentane.

Scheme I



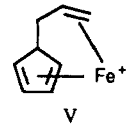
action 12, occurring under activation before the dissociation of the benzene ligand. The lack of an H/D exchange reaction



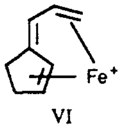
(12)

competing with the condensation suggests that either this process is much slower than the condensation under thermal conditions or it occurs only upon activation. Finally, CID on $Fe(C_6H_6)(C_6D_6)^+$ formed from the successive condensation of Fe^+ with benzene and perdeuterated benzene yields $FeC_6H_6^+$ and $FeC_6D_6^+$, without H/D crossing between the two benzene ligands, consistent with the aforementioned results.

Scheme I is proposed to explain the fragmentation and the extensive isotope scrambling observed in reactions 8–11. This scheme is supported by the following experiments. Fe^+ doubly dehydrogenates allylcyclopentane to form $FeC_8H_{10}^+$, presumably having structure V or VI. CID of this $FeC_8H_{10}^+$ also gives reactions 8–11, with the relative abundances of the different fragments shown in Figure 3. Because of their identical CID fragments and the lack of further characteristic ion–molecule reactions, it is very difficult to show that the two $FeC_8H_{10}^+$ ions from different sources have indeed different structures to start with. The same type of fragmentation processes, coupled with their somewhat different breakdown curves, seem to support the notion that structure V, or its closely related isomer, structure VI, is a key intermediate for the CID of cyclopentadienylallyliron as postulated in Scheme I.



V



VI

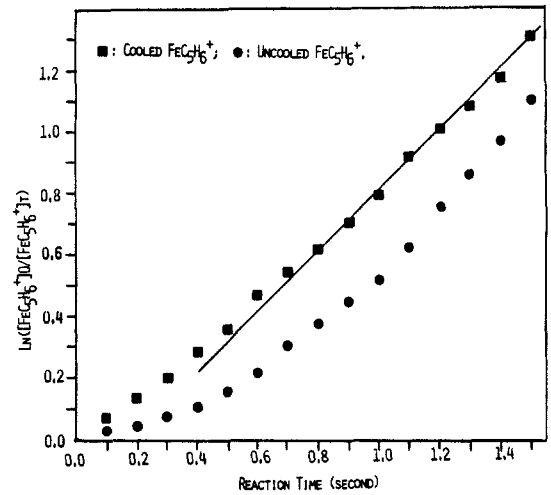


Figure 4. Kinetics plot of cooled and uncooled $FeC_5H_6^+$ with propane.

The direct involvement of the cyclopentadiene ligand in the reaction mechanism is also obvious from the reactions of $FeC_5H_6^+$ with other alkanes. Double dehydrogenation is again observed in its reaction with *n*-butane, forming $CpFe^+$–1-methylallyl, as is supported by the reaction with *n*-butane *1,1,1,4,4,4-d*$_6$, which yields mainly H_2, HD elimination. CID of the ionic product $FeC_9H_7D_5^+$ also gives extensive H/D scrambling. A more interesting reaction is that between $FeC_5H_6^+$ and ethane where monodehydrogenation to give $FeC_7H_{10}^+$ is observed. In contrast, Fe^+ is unreactive with ethane[2] and, thus, the presence of C_5H_6 enhances Fe^+ reactivity. Two structures, $FeCp^+$–ethyl and cyclopentadieneironethylene ion, are reasonable possibilities for this product ion. It has been shown that $FeC_5H_6^+$ undergoes six H/D exchanges with D_2, with the first H/D exchange being significantly faster than the others and with the newly exchanged D atom retaining the endo position in Fe^+–cyclopentadiene.[11] When $FeC_5H_5D^+$ formed from D_2 reacts with ethane, $FeC_7H_{10}^+$ is formed predominantly, suggesting at least initial formation of the cyclopentadienylethyliron ion structure. However, photodissociation of $FeC_7H_{10}^+$ under white light yields elimination of ethylene to give $FeC_5H_6^+$, supporting the latter structure. These results are consistent with the fact that β-hydride transfer is a very facile process, and it is likely that the energy difference between these two structures is very small, thus permitting their interconversion. A similar mechanism is proposed to explain the rapid, six H/D exchanges between $FeC_5H_6^+$ and C_2D_4.[13]

If the hydrido rearrangement process were not possible for $FeC_5H_6^+$, C_5H_6 would be expected to behave essentially as a "spectating" 1,3-diene π ligand. Thus, it is informative to compare this with the chemistry of the structurally similar Fe^+–butadiene. Fe^+–butadiene can easily be prepared from the displacement reaction of butadiene with $FeC_2H_4^+$ and $FeC_3H_6^+$ ions, which are, in turn, prepared from the reaction of Fe^+ with propane. Upon reaction with propane, Fe^+–butadiene yields only the condensation product ion $Fe(C_4H_6)(C_3H_8)^+$. Thus, the absense of a dehydrogenation product for Fe^+–butadiene again supports the importance of hydridocyclopentadienyl intermediate in reaction 5.

Kinetic Studies and the Effect of Excess Internal Energy

In order to provide a qualitative comparison of the reactivities of Fe^+ and $FeC_5H_6^+$ with propane, the pseudo-first-order rate constant between $FeC_5H_6^+$ and propane was measured. At a constant background pressure of propane $\sim 6 \times 10^{-8}$ Torr, the kinetic plot of ln $([FeC_5H_6^+]_0/[FeC_5H_6^+]_t)$ vs reaction time exhibited nonlinear behavior, as shown in Figure 4. For a gas-phase ion–molecule reaction, reactant ions in different electronic states often have quite different reactivities and different reaction cross sections.[14] Although the smooth upward curve observed in Figure

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[13] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 67.

4 can be fit within experimental uncertainty to the logarithm of a biexponential function, we do not believe this to arise due to the presence of an excited electronic state. More likely is that the ions possess some excess internal vibrational or rotational energy. In any event cooling the reactant ions in a background argon pressure of 1×10^{-5} Torr for 500 ms (corresponding to roughly 150 collisions) before monitoring reaction 7 yields more linear behavior, Figure 4. These results indicate that the reaction is sensitive to the reactant ion excess energy, and the direction to which the plot in Figure 4 deviates from linearity indicates that the reaction is exothermic. The rate constant for reaction 7 was determined from several runs to be $5 \pm 2 \times 10^{-10}$ cm^3/(molecule·s), corresponding to a reaction efficiency of about 0.4. This rate constant is substantially larger than that for the reaction of Fe^+ with propane,[15] again demonstrating the enhanced reactivity resulting from the attachment of the cyclopentadiene ligand.

Having attributed the excess energy of the reactant ion as the cause for the observed curvature in the kinetics plot, it leads one to question the origin of this excess energy. One source is the laser-generated Fe^+ reactant ion in reaction 6. Laser desorption is known to generate metal ions that are kinetically and electronically "hot" to some extent,[16] and a portion of this kinetic energy may be carried over to the product ion in reaction 6. In fact, the kinetics plot of uncooled Fe^+ reacting with propane also yields nonlinear behavior. Of greater interest is the possibility that the exothermicity from reaction 6 is in part retained by the product ion and that this might be at least partially responsible for the observed curvature.

While it was extremely difficult to obtain reproducible results to assess the relative importance of the two aforementioned sources, the determination of the exothermicity of reaction 6 should shed some light on the latter source. Normally the determination of a metal ion-ligand bond energy would be straightforward by the usually useful method of ligand bracketing,[17] but it fails here in the determination of $D°(Fe^+–C_5H_6)$ since hydrogen radical is displaced by the incoming ligand, as mentioned earlier for benzene. However, photodissociation provided a successful alternative. Photodissociation of $FeC_5H_6^+$ under white light from the arc lamp at a background argon pressure of about 4×10^{-6} Torr yields about 84% $FeC_5H_5^+$ and 16% Fe^+. By using cutoff filters, the threshold for the appearance of Fe^+ was determined to be at 524 nm, corresponding to $D°(Fe^+–C_5H_6) = 55 \pm 5$ kcal/mol, given the experimental uncertainty. This value is in excellent agreement with $D°(Fe^+–C_5H_6) = 55 \pm 5$ kcal/mol, recently determined by a kinetic energy release measurement,[18] and is consistent with the formation of $FeC_5H_6^+$ from the reaction of Fe^+ with cyclopentane, which indicates that $D°(Fe^+–\text{cyclopentadiene}) > 50$ kcal/mol.[11] For comparison, $D°(Fe^+–\text{butadiene})$ has been reported to be 48 ± 5 kcal/mol.[9] Thus, the exothermicity for reaction 6 is calculated to be 33 ± 5 kcal/mol.[19]

A recent study by Beauchamp and Bowers and co-workers suggests that for H–H bond formation, such as in the dehydrogenation reaction 6, the probability of generating a product ion with a certain amount of kinetic energy decreases with the increasing kinetic energy value, with the maximum kinetic energy release being less than or equal to the reaction exothermicity.[20] Furthermore, their results indicate that probably most of the exothermicity of reaction 6 resides as internal energy in the products. Thus, it is possible that internally excited $FeC_5H_6^+$ accounts in part for the curvature observed in Figure 4.

Finally, it is interesting to note that upon CID, $FeC_5H_6^+$ gives predominantly Fe^+, with only a minor amount of $FeC_5H_5^+$, which decreases in relative abundance as the CID energy increases. This, together with the photodissociation results, signals the appearance of $FeC_5H_5^+$ as a lower energy process than the Fe^+ appearance. The photodissociation threshold for $FeC_5H_6^+$ fragmenting to $FeC_5H_5^+$ occurs at about 622 nm, suggesting $D°(CpFe^+–H) = 46 \pm 5$ kcal/mol, given the experimental uncertainty. The above data can be used with eq 13–15 to determine $D°(Fe^+–Cp)$. From eq 13, $\Delta H_f(FeC_5H_6^+) = 256 \pm 5$ kcal/mol is obtained with use

$$\Delta H_f(FeC_5H_6^+) = \Delta H_f(Fe^+) + \Delta H_f(C_5H_6) - D°(Fe^+–C_5H_6) \tag{13}$$

$$\Delta H_f(FeC_5H_5^+) = D°(FeC_5H_5^+–H) + \Delta H_f(FeC_5H_6^+) - \Delta H_f(H) \tag{14}$$

$$D°(Fe^+–C_5H_5) = \Delta H_f(Fe^+) + \Delta H_f(C_5H_5) - \Delta H_f(FeCp^+) \tag{15}$$

of $\Delta H_f(Fe^+) = 280$ kcal/mol,[19] $\Delta H_f(C_5H_6) = 31 \pm 1$ kcal/mol,[19] and $D°(Fe^+–C_5H_6) = 55 \pm 5$ kcal/mol from above. This value can then be used in eq 14 together with $D°(FeC_5H_5^+–H) = 46 \pm 5$ kcal/mol determined above and $\Delta H_f(H) = 52$ kcal/mol[19] to yield $\Delta H_f(FeC_5H_5^+) = 250 \pm 7$ kcal/mol. Finally, by using $\Delta H_f(C_5H_5) = 58 \pm 1$ kcal/mol,[19] eq 15 yields $D°(Fe^+–C_5H_5) = 88 \pm 7$ kcal/mol. In comparison, $D°(Co^+–Cp) = 85 \pm 10$ kcal/mol has been reported.[21]

Photodissociation Study on Cyclopentadienylallyliron Ion

Photodissociation of $FeC_8H_{10}^+$, generated by reaction 7, using white light from the arc lamp, gives reactions 16 and 17. When $FeC_8H_5D_5^+$ formed from C_3D_8 undergoes photodissociation, reaction 16 gives about 60% HD elimination, along with ~10% D_2 and ~30% H_2 elimination. For reaction 17, the major elimination is $C_2H_2D_2$ at ~60%, along with ~15% C_2HD_3 and ~25% C_2H_3D elimination.

$$FeC_8H_{10}^+ \xrightarrow{h\nu} FeC_8H_8^+ + H_2 \tag{16}$$

$$\rightarrow FeC_6H_6^+ + C_2H_4 \tag{17}$$

More interesting, however, is the dependence of the branching ratio for reactions 16 and 17 on background argon pressure. In this experiment, both cyclopentene and propane were pulsed in sequentially to prepare the photodissociation parent ion, $FeC_8H_{10}^+$. In this way, relatively few ion–molecule collisions could occur during the photodissociation trapping time at 3×10^{-8} Torr in the absence of background argon pressure. Under these conditions, reaction 17 accounts for about 60 ± 5% of the total photodissociation product ions. However, when a background argon pressure of about 1×10^{-5} Torr was present during the photodissociation process, reaction 17 became less important and accounted for only about 46 ± 5% of the total photodissociation product ions, while the total photodissociation efficiency remained the same. The variations of the relative photodissociation cross sections with respect to argon background pressure can be qualitatively explained from the CID breakdown curve in Figure 1. It appears that the parent ion $FeC_8H_{10}^+$ is generated in reaction 7 with some internal energy. As argon background pressure is introduced, it can collisionally remove the excess energy from the parent ion. This is equivalent to moving to the left on the energy axis in Figure 1 (i.e., to lower energies) and, therefore, increasing the relative importance of the lower energy dehydrogenation process. In addition to the two possible sources for the internal energy of $FeC_5H_6^+$, reaction 7 is expected to be a very exothermic process and might also contribute to the internal energy of the parent ions. While instrumental difficulties once again prevented the isolation of each of the above sources of internal energy and the estimate of their relative contributions, this does demonstrate that the

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internal energy of the parent ion can have important effects on the photodissociation process. Similar conclusions have been reached in earlier studies where collisional cooling of the parent ions had an observed effect on the photodissociation thresholds.[22] In addition, a previous study by Dunbar and co-workers indicated that *n*-butylbenzene ion yields fragments *m/e* 91 and 92 upon photodissociation, with the ratio of 91/92 increasing with increasing internal energy of the parent ion.[23]

Conclusion

The study of $FeC_5H_6^+$ and its reaction with several small alkanes reveals some very interesting features. The presence of a cyclopentadiene ligand on Fe^+ has a dramatic effect on the reactivity of Fe^+. The rearrangement of Fe^+–cyclopentadiene to cyclopentadienylhydridoiron enhances reactivity and changes the reaction mechanism. While Fe^+ does not react with ethane, $FeC_5H_6^+$ reacts readily. $FeC_5H_6^+$ also reacts rapidly with propane and *n*-butane to form cyclopentadienylallyliron ion and cyclopentadienyl(methylallyl)iron ion, respectively.

Photodissociation threshold measurements yield $D°(Fe^+–C_5H_6) = 55 \pm 5$ kcal/mol. From this, the reaction exothermicity of Fe^+ dehydrogenation of cyclopentene is calculated to be 33 ± 5 kcal/mol. Some of this energy, along with a fractional portion of the kinetic energy from the laser-generated Fe^+, might reside with the ionic product, $FeC_5H_6^+$, and affects subsequent kinetic behavior. Correct kinetic data can only be obtained by removing the excess energy with background argon.

Photodissociation studies on cyclopentadienylallyliron ion shows that effects on product branching ratios due to internal energy of the parent ion are observed. Without removing the internal energy, the higher energy process forming $FeC_6H_6^+$ is favored. By removing the internal energy with a high pressure of background argon, the lower energy dehydrogenation process forming $FeC_8H_8^+$ is favored.

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Dynamics of the Thermal Dissociation of Unsaturated Cyclic Ketones: Nascent Vibrational Energy Distributions in the Products

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Abstract: It has been found that in thermal dissociation of both norbornenone and 3-cyclopentenone the CO is formed with less than half its statistical share of the energy released from the transition state. We have used (VV) coupling between the products, 1,3-cyclohexadiene and butadiene, respectively, to probe their nascent vibrational energy. They are both born vibrationally excited. It seems that much of the energy released appears as vibrational energy of these molecules. In the transition state the CO group must have a bond length close to that of the free molecule. These results do not permit a decision between symmetric and asymmetric bond cleavage. However, separate experiments in which the rotational distribution has been measured establish that the dissociation does not occur by symmetric bond rupture.

A great deal of research has been conducted in order to discover whether thermal and photochemical dissociation of keto and azo compounds proceeds by the synchronous cleavage of both bonds to the CO or the N_2 groups or sequentially.[1-3] The sequential mechanism has been proved for an unsymmetrical azo compound $CH_3N{=}NR$ by the discovery that in the photochemical dissociation the radical R is formed before the CH_3 and the N_2.[4] However, this is not so surprising considering that the CH_3–N bond is about twice as strong as the R–N bond.[4] Synchronous cleavage is more likely for symmetrical compounds such as $CH_3N{=}NCH_3$, H_2CO, and symmetrical cyclic compounds such as

and

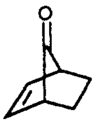
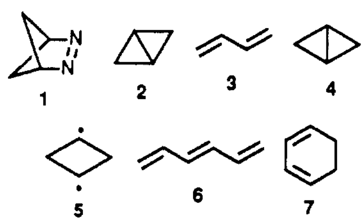


Chart I



Many years ago Bauer suggested that synchronous cleavage could lead to highly vibrationally excited N_2 and CO molecules because of the large changes in the N–N and C–O bond lengths.[5] As pointed out by Engel and co-workers,[6] the degree of vibrational

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