J. Am. Chem. Soc. **1991**, *113*, 4469–4473

Strong Hydrogen Bonding in Gas-Phase Ions. A High-Pressure Mass Spectrometric Study of the Proton Affinity, Proton Transfer Kinetics, and Hydrogen-Bonding Capability of Iron Pentacarbonyl

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Received October 26, 1990. Revised Manuscript Received February 1, 1991

Abstract: Pulsed-ionization high-pressure mass spectrometric investigations of the proton transfer and clustering reactions of protonated iron pentacarbonyl have been carried out. The slow proton transfer kinetics and negative temperature dependence of the reaction with mesitylene are consistent with a barrier to proton transfer within the intermediate ion–molecule complex. Arguments are presented that show that the loss of the fluxional motion in $Fe(CO)_5$ upon protonation leads to an unusually large entropy change. The proton affinity of $Fe(CO)_5$ is determined to be 200.3 kcal mol^{-1}. The clustering of protonated iron pentacarbonyl with acetonitrile is found to be relatively strong at 17 kcal mol^{-1} and is indicative of a hydrogen-bonded complex involving the transition-metal center. Collision-induced decomposition experiments support metal protonation of $Fe(CO)_5$ but ring protonation of ferrocene in the gas phase. This difference in site of protonation is invoked to explain the differences in hydrogen bond strengths in the proton-bound complexes of the two transition-metal species with acetonitrile.

Introduction

Techniques of gas-phase ion chemistry have provided a wealth of experimental data in recent years that has resulted in a greater in-depth understanding of the factors affecting strong hydrogen bonding in both gaseous ions and neutral molecules.[1-5] In particular, correlations of energetics of association of gas-phase ions with neutral molecules that can function as either hydrogen bond donors or acceptors with gas-phase basicity, gas-phase acidity, electronegativity of the heavy-atom participants in the hydrogen bond, and the local environment of the hydrogen-bonding centers have provided a rational means for prediction of hydrogen bond strengths in many situations.[4,5] To date, the gas-phase data on strong hydrogen bonding have generally supported the principle that the heavy-atom participants in a hydrogen bond will be confined to the main-group elements in the upper right hand side of the periodic table. Thus, while there are abundant data on hydrogen bonds involving oxygen and nitrogen and to a lesser extent carbon, fluorine, chlorine, bromine, iodine, and sulphur, no quantitative evidence has been presented to suggest that other elements will participate in hydrogen bonding. However, in view of the ability of the transition elements to form compounds with more than one coordination number, this lack of evidence cannot be taken to indicate that such hydrogen bonding is energetically unfavorable since, for these elements, structures other than hydrogen-bonded ones might be more stable. In addition, the number of investigations carried out on functionalities containing these elements has been significantly fewer than those containing carbon, nitrogen, oxygen, sulphur, or the halogens.

A great deal of attention has been focused on transition-metal coordination chemistry and organometallic chemistry of gaseous ions.[6-10] The studies to date have primarily centered on examination of ligand displacement reactions, oxidative addition and reductive elimination mechanisms, and other qualitative studies of reactivity of the transition-metal species. Until very recently, the only quantitative thermochemical data obtained for gas-phase transition-metal species were relative proton affinities of the neutral molecules[11] and to a limited extent relative binding energies of ions such as $CpNi^+$ to neutral substrates.[12] Both Kebarle[13] and Meot-Ner[14] have now undertaken measurements of the equilibrium proton affinity of ferrocene. In a detailed study of the kinetics of proton transfer to ferrocene, Kebarle has deduced that there is a significant barrier to proton transfer within the complex formed between a variety of protonated bases and ferrocene. From an analysis of the entropy changes that occur upon proton transfer to ferrocene, it was also deduced that ferrocene has significantly higher symmetry than its conjugate acid and that there is a weaker metal–ring interaction in the protonated species. Arguments were also advanced that support the site of protonation in ferrocene as the Fe atom with a possible secondary site on the cyclopentadienyl ring, which is ~10 kcal mol^{-1} less favorable. Meot-Ner's data agree with Kebarle's assignment of the proton affinity of ferrocene as 206 kcal mol^{-1} as well as the slow rate constants for proton transfer. Using deuteration experiments, he has also deduced that there is no scrambling of the added proton with the cyclopentadienyl ring hydrogens. This is taken to support the contention that the site of protonation is either at iron, in an exo ring position or in an agostically bonded position bridging the metal and a ring. Meot-Ner[14] has also examined the binding energetics of protonated ferrocene to acetonitrile. From the very weak binding enthalpy of <8 kcal mol^{-1} obtained, it was concluded that the $-Fe-H^+$ moiety is a poor hydrogen bond donor and that, in general, hydrogen bonds involving iron will be intrinsically weak.

In the course of examination of slow ligand replacement reactions of iron pentacarbonyl by high-pressure mass spectrometry (HPMS) in our laboratory, both the proton affinity of $Fe(CO)_5$ and hydrogen bond energetics of $HFe(CO)_5{}^+$ were determined. The present work details these results and presents evidence, in contrast to Meot-Ner's conclusion, that transition-metal centers can, in fact, participate in moderately strong hydrogen bonding.

Experimental Section

All equilibrium experiments were carried out on a pulsed-ionization high-pressure mass spectrometer constructed at the University of

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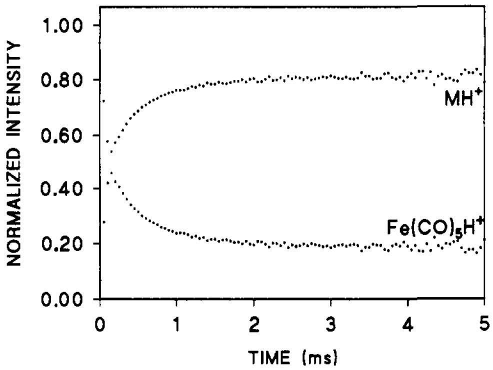

Figure 1. Normalized ionic abundances for protonated $\mathrm{Fe(CO)_5}$ and protonated mesitylene in a mixture of $\mathrm{Fe(CO)_5}$ (16.5 mTorr) and mesitylene (1.4 mTorr) in 4.8 Torr $\mathrm{CH_4}$ at 47 °C.

Waterloo. General principles of high-pressure mass spectrometry have been described in detail elsewhere[15] as have the specific details of the Waterloo apparatus.[16]

Mixtures of iron pentacarbonyl, methane, and other reactive species of interest were prepared in manometrically known ratios in a heated 5-L reservoir. The gaseous mixtures were flowed into the high-pressure ion source to a known pressure (typically ~5 Torr) determined by a Validyne capacitance manometer. Ionization of the gas mixture was effected by a 2-keV beam of electrons, focused by an electron gun onto a 100-μ entrance aperture on the ion source block. The majority of primary ions produced by electron impact are those derived from methane, the major component of the gas mixture. Reactive collisions of these ions lead rapidly to the formation of $\mathrm{CH_5^+}$ and $\mathrm{C_2H_5^+}$, which subsequently react via proton transfer with the minor components of the mixture, which have higher proton affinities than either $\mathrm{CH_4}$ or $\mathrm{C_2H_4}$ (eq 1). Once the protonated species of interest is formed, it may react further by either proton transfer (eq 2) or clustering (eq 3), depending upon the ion source

$$\mathrm{CH_5^+ + M \rightarrow MH^+ + CH_4} \qquad (1a)$$

$$\mathrm{C_2H_5^+ + M \rightarrow MH^+ + C_2H_4} \qquad (1b)$$

$$\mathrm{MH^+ + Fe(CO)_5 \rightarrow HFe(CO)_5^+ + M} \qquad (2)$$

$$\mathrm{MH^+ + Fe(CO)_5 \rightarrow MH[Fe(CO)_5]^+} \qquad (3)$$

conditions and nature of the compound. The chemical ionization reagent gas methane also functions as an inert buffer for the product ions and is present in sufficiently large excess that all ions undergo rapid thermalization prior to reaction. Under typical ion source conditions, ion-molecule collision frequencies of ~10^8 $\mathrm{s^{-1}}$ are obtained. Ions emerging from the ion source through a second 100-μ aperture are accelerated to 2 keV, focused, and magnetically mass analyzed. The ionizing electron beam is pulsed, and the gate for this pulse is also used to trigger a multichannel analyzer such that the intensity profile of a mass-selected ion beam can be followed for up to several tens of milliseconds.

Equilibrium constants for proton transfer and clustering reactions are obtained from the steady-state abundances at long ion source residence times and the known partial pressure ratio of reference base and $\mathrm{Fe(CO)_5}$ (for proton affinity measurements) or the absolute pressure of substrate (for clustering measurements). These equilibria are then examined as a function of ion source temperature, and from plots of ln K_{eq} vs T^{-1} (Van't Hoff plot) both the enthalpy and entropy changes for reaction can be determined. Due to the limited thermal stability of $\mathrm{Fe(CO)_5}$, all experiments were carried out below 150 °C.

Collision-induced decomposition (CID) experiments as well as reactivity studies of isotopically labeled isolated ions were carried out on a Bruker Spectrospin CMS 47 Fourier transform ion cyclotron resonance (FT-ICR) spectrometer equipped with an external high-pressure source. This apparatus is also described in detail elsewhere.[17]

Methane, used as the bath gas of 99.999% purity, was obtained from Matheson Canada Ltd. Iron pentacarbonyl and all other reagents were obtained from Aldrich in highest purity available and were used without further purification.

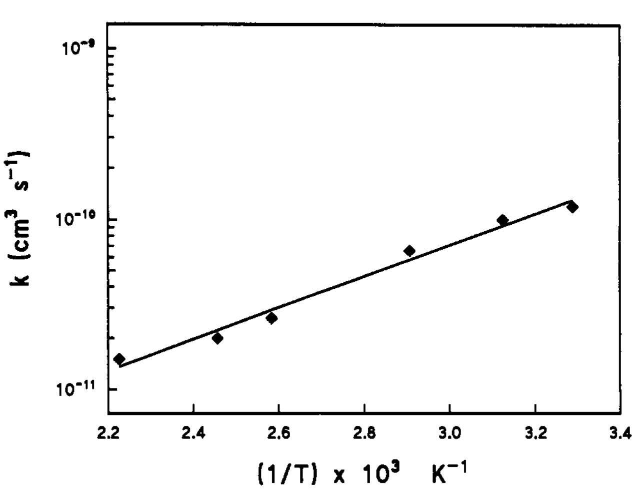

Figure 2. Variation of the rate constant for proton transfer from $\mathrm{HFe(CO)_5^+}$ to mesitylene (eq 4) with reciprocal temperature.

Results and Discussion

The only previously published determination of the proton affinity or iron pentacarbonyl establishes its gas-phase basicity as less than that of $\mathrm{NH_3}$ but greater than that of $\mathrm{(CH_3O)_2CO}$.[19] With use of the currently accepted NBS proton affinity scale,[18] this allows the proton affinity of $\mathrm{Fe(CO)_5}$ to be assigned as 202 ± 2 kcal $\mathrm{mol^{-1}}$. In order to obtain an accurate equilibrium proton affinity, the proton transfer equilibrium was examined for mixtures of iron pentacarbonyl and mesitylene. A typical example of variation of the normalized ionic abundances with reaction time is displayed in Figure 1 for a mesitylene–$\mathrm{Fe(CO)_5}$ mixture. It is readily apparent from the data that proton transfer equilibrium is established only after approximately 2000 μs, indicating that the reaction is proceeding in the exothermic direction at considerably less than the ion–molecule collision rate. This is consistent with the kinetic observations of Kebarle[13] and Meot-Ner[14] of slow proton transfer kinetics between protonated carbon bases and ferrocene. In order to quantify this observation, the rate constant for proton transfer from protonated $\mathrm{Fe(CO)_5}$ to mesitylene was investigated by examining the initial rate of disappearance of $\mathrm{HFe(CO)_5^+}$ as a function of time after the electron gun pulse in mixtures with a high ratio of mesitylene to $\mathrm{Fe(CO)_5}$ but at very low partial pressures of both. The variation of the rate constant for proton transfer from protonated iron pentacarbonyl to mesitylene (reaction 4, where values under each compound refer to rotational symmetry numbers (σ)) with temperature, shown in

$$\underset{4}{\mathrm{HFe(CO)_5^+}} + \underset{6}{\mathrm{C_6H_3(CH_3)_3}} \rightleftharpoons \underset{2}{\mathrm{C_6H_3(CH_3)_3H^+}} + \underset{6}{\mathrm{Fe(CO)_5}} \qquad (4)$$

Figure 2, reveals a negative temperature dependence consistent with an internal barrier to proton transfer within the intermediate ion–molecule complex. As discussed by Kebarle,[13] this type of behavior is anticipated in reactions involving carbon bases such as mesitylene where formation of the ion–molecule complex leads to loss of resonance stabilization.

The proton transfer equilibrium involving $\mathrm{Fe(CO)_5}$ and mesitylene was also examined in detail as a function of temperature to determine accurately both the enthalpy and entropy changes for proton transfer. The latter quantity was deemed to be of some interest in order to assess whether there was an unusually large unfavorable entropy change associated with protonation of $\mathrm{Fe(CO)_5}$ arising from the change from a fluxional trigonal-bipyramidal $\mathrm{Fe(CO)_5}$ to a rigid octahedral $\mathrm{HFe(CO)_5^+}$ structure. The

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Table I. Thermochemical Data Derived from Clustering and Transfer Equilibria

reaction	ΔH^a	ΔS^b
$HFe(CO)_5^+ + C_6H_3(CH_3)_3 \rightleftharpoons C_6H_3(CH_3)_3H^+ + Fe(CO)_5$	-0.7	5.5
$HFe(CO)_5^+ + CH_3CN \rightleftharpoons CH_3CN\cdots H^+\cdots Fe(CO)_5$	-16.8	-26.8
$CH_3CN\cdots H^+\cdots Fe(CO)_5 + CH_3CN \rightleftharpoons [CH_3CN]_2H^+ + Fe(CO)_5$	-1.5	-4.0
$CH_3CNH^+ + CH_3CN \rightleftharpoons [CH_3CN]_2H^+$	-28.9^c	-27.2^c

[a] ±0.2 kcal/mol. [b] ±2 cal/(mol·K). [c] These values are in good agreement with those obtained by Meot-Ner (*J. Am. Chem. Soc.* **1978**, *100*, 4694).

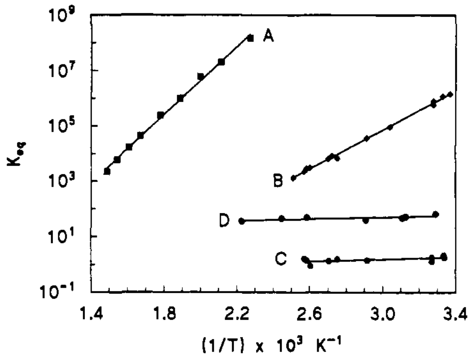


Figure 3. Van't Hoff plots for clustering and proton transfer reactions: A, eq 7; B, eq 5; C, eq 6; D, eq 4.

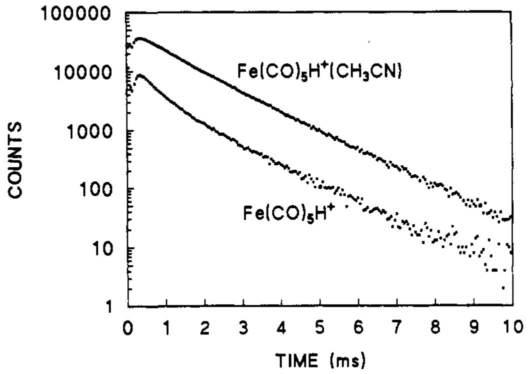
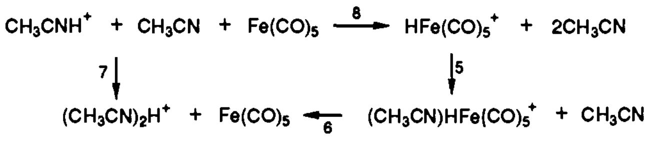


Figure 4. Experimental ionic abundances of protonated $Fe(CO)_5$ and its association complex with acetonitrile in a mixture of $Fe(CO)_5$ (37 mTorr) and CH_3CN (11.5 mTorr) in 5 Torr CH_4 at 94 °C.

Scheme I



temperature dependence of the proton transfer equilibrium constant, shown in Figure 3, yields ΔH_4 of -0.7 kcal mol^{-1} and ΔS_4 of 5.5 cal mol^{-1} K^{-1}. Taking values of rotational symmetry numbers (σ) for the species in reaction 4 as indicated, the entropy change associated with the net overall symmetry change in going from reactants to products can only account for 1.4 cal mol^{-1} K^{-1} of the observed entropy change, thus leaving 4 cal mol^{-1} K^{-1} to be accounted for. This magnitude of entropy change, while not unprecedented for proton transfers, is nevertheless larger than normally observed. The fluxional motion of $Fe(CO)_5$ is known to be on the order of 10^{10} s^{-1}, faster than the NMR time scale but slower than the infrared time scale. If this fluxional motion is treated as a low-frequency vibration or hindered rotation, statistical thermodynamic considerations dictate that this motion will add a large contribution to the entropy of the neutral transition-metal compound. Loss of this motion in the ion, in the absence of new low-frequency modes, would then lead to the prediction that protonation of $Fe(CO)_5$ would be unusually entropically unfavorable. Microwave dielectric relaxation measurements[20] have shown that the frequency of the Berry pseudorotational motion of iron pentacarbonyl is likely in the vicinity of 5 cm^{-1}. Treating this statistically as a low-frequency molecular vibration in the molecular partition function gives an entropy associated with such a motion of ~7.4 cal mol^{-1} K^{-1}. If it is assumed that there is some low-frequency motion of the newly formed octahedral protonated iron carbonyl to partially compensate for the loss of the Berry pseudorotation, then the remaining 4 cal mol^{-1} K^{-1} entropy change for eq 4 might be explained on the basis of gain of the fluxional motion of the trigonal-bipyramidal neutral molecule. It would obviously be of considerable interest to test this hypothesis by examination of entropy changes for protonation of other trigonal-bipyramidal species with even lower frequencies of pseudorotation. Interestingly, such species have recently been synthesized and their fluxional interconversions characterized in the form of osmium compounds containing mixed CO and C_2H_4 ligands.[21]

The temperature dependence of the equilibrium constant for reaction 4 combined with the temperature dependence of the rate constant for reaction in the forward direction allows the rate constant for reaction in the reverse direction to be calculated. It is noteworthy that this reverse reaction then also has a negative temperature dependence, consistent with a model for proton transfer with an intermediate barrier somewhat below the energies of both reactants and products.

The value of ΔH_4 of -0.7 kcal mol^{-1}, taken with Stone's value for the proton affinity of mesitylene of 201.0 kcal mol^{-1},[22] establishes the proton affinity of $Fe(CO)_5$ as 200.3 kcal mol^{-1}, in good agreement with the approximate value previously obtained from ICR bracketing experiments of 202 ± 2 kcal mol^{-1}.

Kebarle has conjectured that a significant barrier to proton transfer within the intermediate complex for proton transfer to ferrocene, and hence the slow kinetics, arises from an inherently poor ability by Fe to participate in hydrogen bonding. Data obtained by Meot-Ner[14] for the energetics of interaction of protonated ferrocene with acetonitrile appear to support this conclusion. In order to determine whether this supposed poor ability to hydrogen bond was evident in iron pentacarbonyl, an investigation of the hydrogen bond energetics involving $Fe(CO)_5$ was undertaken.

A typical example of variation of ion intensities with time is shown in Figure 4 for a mixture of $Fe(CO)_5$ and CH_3CN. A Van't Hoff plot for the resulting clustering equilibrium (eq 5) is shown in Figure 3. In addition to $HFe(CO)_5^+$ and its addition complex with CH_3CN, the proton-bound dimer of acetonitrile, $(CH_3CN)_2H^+$, was also observed to be apparently in equilibrium with these ions. Since no protonated acetonitrile is observed, the equilibrium must involve a CH_3CN exchange reaction between $HFe(CO)_5^+$ and CH_3CNH^+ (eq 6). A Van't Hoff plot for this equilibrium is also included in Figure 3. In order to observe the clustering equilibrium of CH_3CNH^+ with CH_3CN (eq 7), experiments were carried out at higher temperatures in the absence of $Fe(CO)_5$. The results obtained are also presented in Figure

$$HFe(CO)_5^+ + CH_3CN \rightleftharpoons CH_3CN\cdots H^+\cdots Fe(CO)_5^+ \quad (5)$$

$$CH_3CN\cdots H^+\cdots Fe(CO)_5^+ + CH_3CN \rightleftharpoons [CH_3CN]_2H^+ + Fe(CO)_5 \quad (6)$$

$$CH_3CNH^+ + CH_3CN \rightleftharpoons [CH_3CN]_2H^+ \quad (7)$$

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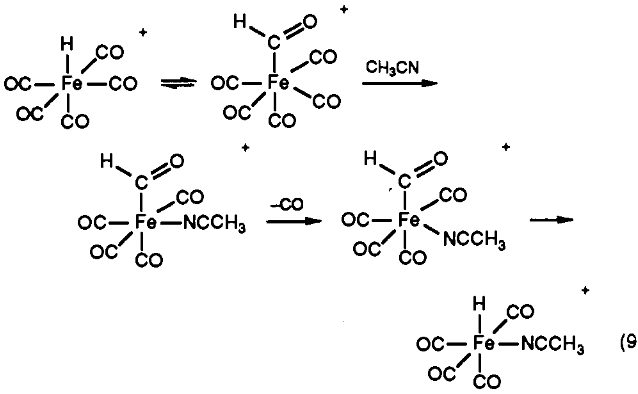
3, and the thermochemical data derived from each of these plots are summarized in Table I. These data show that, in contrast to the very weak interaction observed by Meot-Ner between Cp_2FeH^+ and CH_3CN of ~8 kcal mol^{-1}, the association of $HFe(CO)_5^+$ with CH_3CN is quite strong at ~17 kcal mol^{-1}.

Consideration of the data in Table I allows the construction of the thermochemical cycle (Scheme I) and permits the calculation of the proton affinity difference between CH_3CN and $Fe(CO)_5$. This calculation yields a value of −13.0 kcal mol^{-1} for the enthalpy change for proton transfer between these two bases (eq 8). This, combined with the established proton affinity of

$$CH_3CNH^+ + Fe(CO)_5 \rightleftharpoons HFe(CO)_5^+ + CH_3CN \quad (8)$$

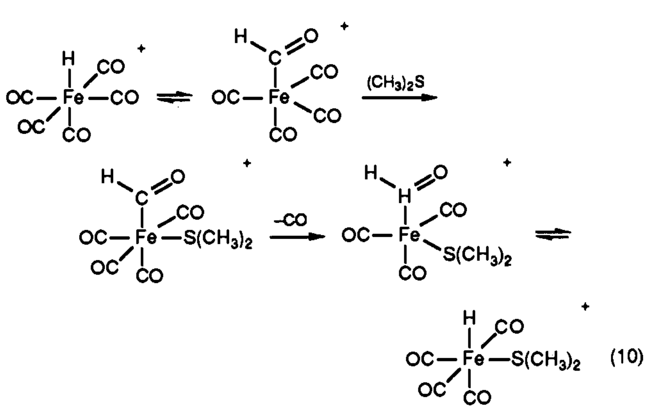
acetonitrile of 187.7 kcal mol^{-1}, permits the proton affinity of iron pentacarbonyl to be calculated as 200.7 kcal mol^{-1}, in excellent agreement with the value determined by direct proton transfer equilibrium with mesitylene. In addition, this excellent agreement for the proton affinity data lends considerable confidence to the level of accuracy of the thermochemical data used to construct Scheme I.

The magnitude of the interaction determined between protonated $Fe(CO)_5$ and CH_3CN suggests that either the hydrogen-bonding ability of iron is greater than previously presumed or that a structure other than a hydrogen-bonded one is being produced. By analogy to the known reactions of the isoelectronic $HMn(CO)_5$,[23] it might be suggested that a hydride migration is taking place, thus creating a vacant coordination site on the iron, which is subsequently able to bind the CH_3CN (eq 9). This possibility can likely be ruled out however on the basis of the failure to observe CO displacement by CH_3CN, either under HPMS conditions or under the considerably lower pressure conditions of analogous ICR experiments, which have previously been carried out. By contrast, exothermic ligand replacement reactions are a dominant feature of coordinately unsaturated $Fe(CO)_n^+$ ions.[32] There is however some evidence in our parallel studies of protonated $Fe(CO)_5$ with poorer hydrogen bonding bases, such as sulfides, that a very slow ligand replacement reaction does proceed that can most readily be rationalized on the basis of a slow unimolecular hydride migration followed by a fast bimolecular addition of sulfide with loss of CO and back-migration of hydride (eq 10).[24] This process is in fact repeated several times until only a single CO remains bound to the iron center. When a more strongly hydrogen bonding substrate is used, the slow unimolecular hydride migration is not observed because of the fast occurrence of termolecular clustering to form a hydrogen-bonded adduct. Thus, with ethers, the oxygen analogue of sulfides, only adduct formation is seen and no CO replacement reaction is observed.



(9)

The strength of the hydrogen bond between $HFe(CO)_5^+$ and CH_3CN can be used to assess the intrinsic ability of an iron center to participate in ionic hydrogen bonds. The bond strength of 16.7 kcal mol^{-1} can be compared to the strength of the hydrogen bond between NH_4^+ and CH_3CN of 27 kcal mol^{-1} and that between protonated aniline and CH_3CN of 17 kcal mol^{-1}.[25] There is a well-known general decrease in hydrogen bond strength with increasing proton affinity difference between the bond participants.[26,27] within a homologous series of compounds. The proton affinity difference between $Fe(CO)_5$ and CH_3CN of 13 kcal mol^{-1} is slightly less than that between NH_3 and CH_3CN of 16 kcal mol^{-1}, while the former hydrogen bond strength is 10 kcal mol^{-1} weaker. The proton-bound dimer strengths of aniline and $Fe(CO)_5$ with CH_3CN are essentially identical despite the fact that the former pair has a proton affinity difference that is 10 kcal mol^{-1} greater. These comparisons show that iron is therefore an intrinsically poorer hydrogen bond participant than is nitrogen, a not surprising result given that nitrogen is a commonly known hydrogen-bonding atom. Clustering data obtained by Meot-Ner for proton-bound dimers of nitrogen and sulfur bases[26] show that, for a proton affinity difference of 13 kcal mol^{-1}, a hydrogen bond strength of ~18 kcal mol^{-1} is expected. This would then suggest that iron is comparable to sulfur in its ability to participate in gas-phase ionic hydrogen bonds. The hydrogen bond strength in the proton-bound dimer of $(CH_3)_2S$ of 16 kcal mol^{-1} would then suggest that the symmetric proton-bound dimer of $Fe(CO)_5$ might also be observed.



(10)

In view of the large difference between the protonated iron pentacarbonyl and protonated ferrocene bond strengths to CH_3CN, the question must be asked as to why the latter pair should form such a significantly weaker hydrogen bond. One possible interpretation of this difference may lie in a consideration of the preferred sites of protonation of iron pentacarbonyl and ferrocene. On the basis of solution-phase NMR data and molecular orbital arguments, it has previously been concluded that iron pentacarbonyl is protonated on Fe both in solution[28,29] and in the gas phase.[30] However, some ambiguity remains concerning the site of protonation of ferrocene. The first NMR studies of ferrocene in strongly acidic solutions[31] showed that ferrocene was evidently metal-protonated and that all of the ring hydrogens remained equivalent. It was on this basis that both Kebarle and Beauchamp presumed in their HPMS[13] and ICR[32] studies of protonated ferrocene that iron protonation also occurred in the gas phase. Meot-Ner concluded, based on failure to observe hydrogen scrambling in deuteration experiments, that either Fe protonation or some other unique site protonation was occurring.[14] However, more recent investigations of ferrocene protonation in a variety of media[33,34] have concluded that both metal and ring protonation can occur, with the site of protonation dependent on the nature

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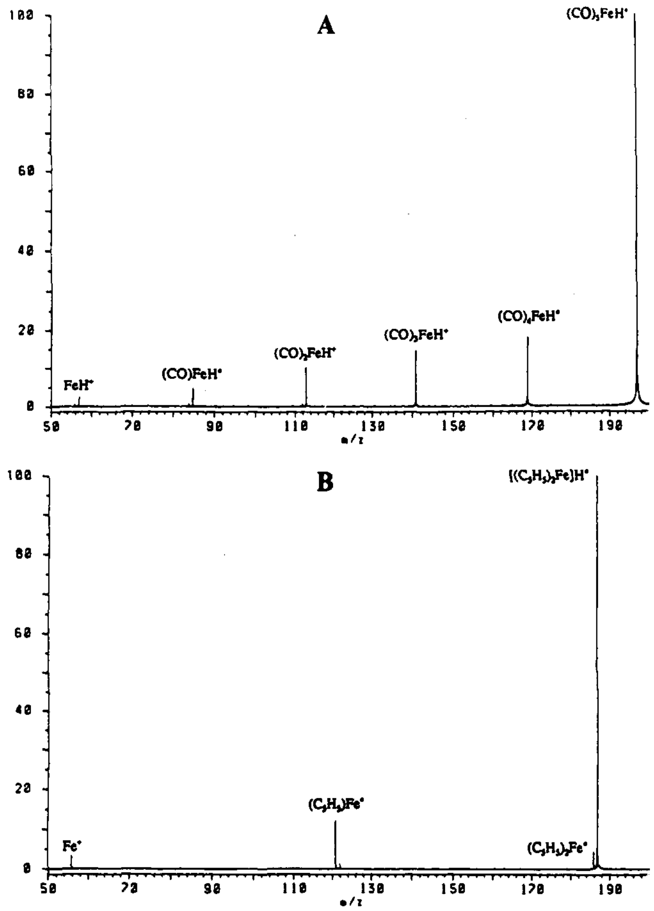

Figure 5. FT-ICR collision-induced decomposition mass spectra of A, protonated $Fe(CO)_5$ and B, protonated ferrocene at a center-of-mass energy of 12.0 eV and a CID delay of 100 ms in 4×10^{-8} Torr of Ar.

of the medium. In particular, in weakly acidic, aprotic media, it appears that, in fact, the cyclopentadienyl ring is preferrentially protonated. This is consistent with the frequently observed discrepancy between relative basicities in the gas phase vs solution that arises because of the dramatic reduction in solvation energies that occur in highly charge delocalized species.

In view of the solution-phase preference for ring protonation in aprotic media and the much weaker hydrogen bond energy observed in the gas phase for ferrocene compared to that for iron pentacarbonyl, it appears highly probable that ring protonation of ferrocene may also be occurring in the gas phase. The failure to observe isotope scrambling[14] dictates that the ring protonation must take place in such a way that the added hydrogen is different from all other ring hydrogens. Meot-Ner has suggested that exo ring protonation may be followed by an agostic $Fe–H^+$ bridge formation. An alternative interpretation may then be that, in view of the fact that Fe-protonated ferrocene in solution is observed to have tilted rings,[35] the proton on iron may be effectively shielded by the π cloud of the rings, thus preventing effective hydrogen bond formation with added base and substantially reducing the rate of proton transfer by making the proton so inaccessible.

In order to provide some insight into the structure of these protonated iron compounds in the gas-phase, collision-induced dissociation (CID) experiments were carried out in a FT-ICR spectrometer. The protonated Cp_2Fe and $Fe(CO)_5$ were generated in an external high-pressure source as described elsewhere[17] and then transferred to the ICR cell where low energy CID with Ar as the collision gas was carried out. The two CID mass spectra are shown in Figure 5. The spectrum of $HFe(CO)_5^+$ reveals almost exclusive loss of CO units, even under multiple collision conditions. Although at higher ion energies a small amount of Fe^+ is observed, this is very probably the result of secondary fragmentation of the more abundant FeH^+. The absence of any significant loss of H-containing neutral fragments gives a strong indication that, as expected, $Fe(CO)_5$ is indeed iron-protonated. In contrast, the CID mass spectrum of $[Cp_2Fe]H^+$ gives strong indications that protonation may not be occurring at the metal. The most prominent fragmentations of $[Cp_2Fe]H^+$ observed are loss of cyclopentadiene, C_5H_6, and loss of H, to yield m/z 121 and 186, respectively. Experiments were also carried out in which either *tert*-butyl chloride-d_9 or D_2O was added to the high-pressure source in sufficient amount to yield an intense deuterated ferrocene ion, $[Cp_2Fe]D^+$, signal. In these cases, loss of C_5H_5D was favored over C_5H_6 loss by a ratio of $\sim$2:1 in the CID mass spectrum. Quite surprisingly loss of H was significantly more abundant than loss of D (>10:1), in apparent contradiction with the proton/deuteron transfer experiments of Meot-Ner[14] in which only transfer of the added deuterium to bases of higher proton affinity was supposedly observed. In order to check Meot-Ner's proton transfer conclusion, an experiment was carried out in which deuteronated ferrocene, generated in the external high-pressure source, was isolated and trapped in the ICR cell and allowed to react with methylamine, which has a proton affinity roughly 6 kcal mol^{-1} greater than that of ferrocene. Consistent with the CID experiment, transfer of a proton was favored over transfer of a deuteron by a ratio of approximately 5:3. This result and the facile loss of cyclopentadiene strongly suggests that protonation occurs on the ring or at least in an agostically bonded position bridging the ring and the metal such that some ring hydrogens become labile toward proton transfer.[36] Such a conclusion would also explain the substantial differences in the ability of the two transition-metal compounds to bind acetonitrile. In the case of protonated iron pentacarbonyl, a true hydrogen bond between Fe and the nitrogen is formed, whereas in the case of ferrocene the adduct involves a proton bridge between a carbon and a nitrogen center.

Conclusions

The kinetics and energetics of protonation of $Fe(CO)_5$ have been presented. The kinetic data reveal that a significant barrier to proton transfer exists within the intermediate proton-bound complex of iron pentacarbonyl and mesitylene. This is reminiscent of the behavior of similar complexes involving ferrocene and carbon bases. Proton transfer equilibria between mesitylene and $Fe(CO)_5$ yield a proton affinity of the transition-metal compound of 200.3 kcal mol^{-1}. A thermochemical cycle involving acetonitrile and $Fe(CO)_5$ allows calculation of the proton affinity as 200.7 kcal mol^{-1}. The excellent agreement between the two methods lends considerable confidence to the accuracy of the experimental procedure as well as the associated clustering thermochemistry. These latter data give a significant hydrogen bond strength in the mixed proton-bound dimer of $Fe(CO)_5$ and CH_3CN of 17 kcal mol^{-1}. This is substantially greater than the strength of the analogous hydrogen bond formed between ferrocene and CH_3CN, which suggests that the latter transition-metal compound may not in fact be iron-protonated. Collision-induced decomposition and deuterium-labeling experiments in $HFe(CO)_5^+$ and Cp_2FeH^+ support metal protonation of $Fe(CO)_5$ and ring protonation of Cp_2Fe.

Acknowledgment. Financial support of the Natural Sciences and Engineering Research Council of Canada and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. $Fe(CO)_5$, 13463-40-6; CH_3CN, 75-05-8.

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