

# Ion Chemistry of Ferrocene. Thermochemistry of Ionization and Protonation and Solvent Clustering. Slow and Entropy-Driven Proton-Transfer Kinetics

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**Abstract:** The ionization energy of ferrocene ( $\text{Cp}_2\text{Fe}$ ) was measured by charge-transfer equilibria as  $6.81 \pm 0.07$  eV ( $157.1 \pm 1.6$  kcal/mol). The proton affinity was obtained from equilibrium temperature studies as  $207 \pm 1$  kcal/mol. The protonation of  $\text{Cp}_2\text{Fe}$  also involves a significant entropy change of  $+6.3$  cal/mol·K. Deuteration experiments show that, in the protonation of  $\text{Cp}_2\text{Fe}$ , the incoming proton goes to a sterically unique position and does not exchange with the ring protons. This is consistent with protonation on iron, but ring protonation exclusively in an exo position or an agostic ring-to-iron bridged structure are also possible. The results suggest that the proton affinity at Fe is greater by at least 5 kcal/mol than for ring protonation. The solvation energies of  $\text{Cp}_2\text{Fe}^+$  and  $\text{Cp}_2\text{FeH}^+$  by a  $\text{CH}_3\text{CN}$  molecule, 11.4 and 12.9 kcal/mol, respectively, are weaker than those of most gas-phase cations, and the attachment energies of dimethyl ether and benzene,  $<9$  kcal/mol, are even weaker. These results support that the weak solution basicity of  $\text{Cp}_2\text{Fe}$  is due to inefficient ion solvation. The kinetics of proton transfer between  $\text{Cp}_2\text{Fe}$  and some cyclic compounds is unusually slow, with reaction efficiencies of 0.1–0.01, without significant temperature dependence. These are the first proton-transfer reactions to show such behavior, which may be due to a combination of an energy barrier and steric hindrance. Proton transfer is also observed from  $(\text{RCN})_2\text{H}^+$  dimer ions to  $\text{Cp}_2\text{Fe}$ . These reactions may be direct or involve ligand switching, and in several cases either mechanism is endothermic and entropy-driven.

Gas-phase studies of ions allow the measurement of intrinsic solvent-free energies and reactivities. Mass spectrometric studies of the gas-phase interactions of metal ions with organic molecules are therefore of active current interest. On the other hand, solvation affects extensively the condensed-phase ion chemistry of organometallics and plays a critical role in electrochemistry and electron-transfer reactions. Therefore, the interaction energies of organometallic ions with individual solvent molecules and small clusters are also of interest.

Ion thermochemistry, and especially solvent clustering to ions, can be measured efficiently by pulsed temperature-variable high-pressure mass spectrometry. This technique has been very successful in measuring the ion thermochemistry and clustering of organics and inorganics<sup>1,2</sup> but has not been as yet applied to the ion chemistry of organometallics.

Ferrocene (denoted below as  $\text{Cp}_2\text{Fe}$ ) is a prototype organometallic complex. Despite this, the fundamental ion thermochemistry is still not defined accurately. Thus, the published ionization energies were obtained by electron ionization<sup>3,4</sup> or from diffuse ionization onset by photoionization<sup>5</sup> and photoelectron spectroscopy,<sup>6–11</sup> and the values range over  $\pm 4$  kcal/mol.

The proton affinity of  $\text{Cp}_2\text{Fe}$  has been determined only in one bracketing measurement, based on relative free energies of protonation, with an uncertainty of  $\pm 4$  kcal/mol.<sup>12</sup> These measurements were done at one temperature, without measuring the

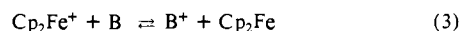
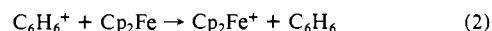
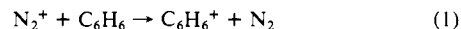
associated entropy changes. In any event, the results revealed that the intrinsic basicity is strong, being between ammonia and methylamine. This is much higher than may be expected from the weak solution basicity, and the comparison suggests that ionized ferrocene is very weakly solvated. However, the interaction energies of the  $\text{Cp}_2\text{Fe}^+$  and  $\text{Cp}_2\text{FeH}^+$ , or indeed of any organometallic ions, with solvent molecules have not been measured.

Given the present status of the data, it is desirable that the IP and PA values will be verified and refined by an independent equilibrium technique and that the application of pulsed high-pressure mass spectrometry to the ion clustering of organometallics be explored. The present work deals with these subjects.

## Experimental Section

The measurements were performed by the NBS pulsed high-pressure mass spectrometer and standard techniques.<sup>13</sup> Ferrocene was dissolved in benzene or methanol in a known concentration, and the solution was injected into a heated bulb. For IP measurements by charge-transfer equilibria, nitrogen was used as a carrier gas, and a reference compound with known IP was also added. In a typical mixture, nitrogen was 98%, benzene 1–2%, and ferrocene and the reference compound  $<0.1\%$ . The concentrations of ferrocene and the reference compounds were calculated from the known mixture compositions and were known within  $\pm 10\%$ . The concentration of ferrocene was verified by the observed rates of protonation and charge-transfer reactions, which proceeded at unit collision efficiency when calculated by the nominal concentration. The total source pressure was 1–2.5 Torr.

Under these conditions, pulsed electron impact generates mostly  $\text{N}_2^+$  ions, and reactant ions are generated mostly by the fast chemical ionization sequence



where B is the reference compound. The third reaction is the equilibrium of interest. Under our conditions equilibrium is achieved in less than 1 ms and is observed for a further 2–4 ms. The sequence of reactions assures that the main ionizing agent is  $\text{C}_6\text{H}_6^+$ , and therefore the  $\text{Cp}_2\text{Fe}^+$  ions are generated by relatively mild charge transfer. In addition, during the observed reaction time the ions undergo over 10 000 collisions with the carrier gases. This assures that the system is thermalized, and no ions

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Table I. Ion Thermochemistry<sup>a</sup> of Ferrocene Reactions with Reference Compounds or Ligands B

B	$\Delta H^\circ$	$\Delta S^\circ$	$\Delta G^\circ(T)$	IP(B) <sup>b</sup> or PA(B) <sup>a</sup>	IP(Cp <sub>2</sub> Fe) or PA(Cp <sub>2</sub> Fe)
Charge-Transfer Reactions B <sup>+</sup> + Cp <sub>2</sub> Fe → Cp <sub>2</sub> Fe <sup>+</sup> + B					
1. DMT <sup>d</sup>	-3.0	1.0		159.8	156.8
2. DET <sup>d</sup>	-0.1	2.2		157.5	157.4
				av	157.1 ± 1
Proton-Transfer Reactions BH <sup>+</sup> + Cp <sub>2</sub> Fe → Cp <sub>2</sub> FeH <sup>+</sup> + B					
3. pyrrole	2.2	5.6	-1.2 (600)	208.6	206.4
4. 1,4-diazine	1.8	4.2	-0.70 (600)	209.0	207.2
5. 2-fluoropyridine	3.6	6.2	-0.1 (600)	210.6	207.0
6. 3-fluoropyridine	7.0	10.6	0.6 (600)	214.3	207.3
				av	207.0 ± 1
Clustering Reactions Cp <sub>2</sub> Fe <sup>+</sup> + B → Cp <sub>2</sub> Fe <sup>+</sup> ·B					
7. CH <sub>3</sub> CN	-11.4	-18.9			
8. 2CH <sub>3</sub> CN <sup>e</sup>	-9.1	-16.0			
9. (CH <sub>3</sub> ) <sub>2</sub> O	>-9	(-20) <sup>f</sup>	>-3.7 (250)		
10. C <sub>6</sub> H <sub>6</sub>	>-8	(-20) <sup>f</sup>	>-3.0 (252)		
11. DMT <sup>d</sup>	-12.2	-20.6			
12. Cp <sub>2</sub> Fe	>-12	(-20) <sup>f</sup>	>-6.9 (253)		
13. Cp <sub>2</sub> FeH <sup>+</sup> ·CH <sub>3</sub> Cn	-12.9	-23.4			

<sup>a</sup> Units of kcal/mol and cal/mol·K. *T* in K. <sup>b</sup> Reference 14. <sup>c</sup> Reference 15. <sup>d</sup> DMT = *N,N*-dimethyl-4-toluidine; DET = *N,N*-diethyl-4-toluidine. <sup>e</sup> For the reaction Cp<sub>2</sub>Fe<sup>+</sup>·CH<sub>3</sub>CN + CH<sub>3</sub>CN. <sup>f</sup> Estimated.

in electronically excited states are present.

For proton-transfer equilibria CH<sub>4</sub> was used as the carrier gas. A total of 2–20% CH<sub>3</sub>OH was also added to the reaction system. Here, fast reactions yield CH<sub>3</sub>OH<sub>2</sub><sup>+</sup> and CH<sub>3</sub>OH<sub>2</sub><sup>+</sup>·*n*CH<sub>3</sub>OH as protonating ions.

In clustering experiments of Cp<sub>2</sub>Fe<sup>+</sup> with CH<sub>3</sub>CN, 0.1–0.4% CH<sub>3</sub>CN was added to the reaction mixture as well as 0.01% (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N. The latter was added as a proton trap to ensure that any Cp<sub>2</sub>FeH<sup>+</sup> generated by side reactions was removed, and therefore low-resolution and high-sensitivity mass analysis could be used.

The Cp<sub>2</sub>Fe sample was a sublimation purified sample and donated by Dr. D. Richardson. The other compounds were of commercial sources and of purity >98% and were used as purchased.

## Results and Discussion

**1. Ionization Energy.** The ionization energy of Cp<sub>2</sub>Fe is low and in a range where few convenient reference compounds fall. Fortunately, however, the IPs of aniline derivatives are in this range, and the ionization energies of a series of these compounds were measured by charge-transfer equilibria.<sup>14</sup> In the present work we use *N,N*-dimethyl-*p*-toluidine (DMT) and *N,N*-diethyl-*p*-toluidine (DET) as reference compounds. The IPs of these compounds were measured previously as 6.93 and 6.83 eV, respectively, also by equilibrium methods.<sup>14</sup> The error in  $\Delta H^\circ$  from equilibrium measurements is usually less than ±1.0 kcal/mol (0.04 eV). The equilibrium IPs of the reference compounds were referenced to *N,N*-dimethylaniline, which was measured as 7.12 ± 0.01 eV (164.2 ± 0.2 kcal/mol). Therefore, the IPs of the reference compounds can be considered accurate within ±0.05 eV. Also in relation to the equilibrium values, it is noted that the measurements were made at 300 K or higher, but the IP of the reference standard, from spectroscopic measurements, relates to 0 K. However, it has been shown that the difference between the heat capacities of the ions and respective neutrals between 0 K and the ambient temperatures is negligible for aromatic molecules, and therefore all the equilibrium values closely approximate the 0 K IPs.<sup>14</sup>

The charge-transfer equilibria 1 and 2 in Table I were measured as a function of temperature. van't Hoff plots were constructed (Figure 1 and 2), and the results are shown in Table I. From the  $\Delta H^\circ$  of the two measurements, the IP of Cp<sub>2</sub>Fe is obtained as 6.78 and 6.82 eV (156.3 and 157.4 kcal/mol). Combining the usual error of  $\Delta H^\circ$  measurements of ±0.04 eV with the uncer-

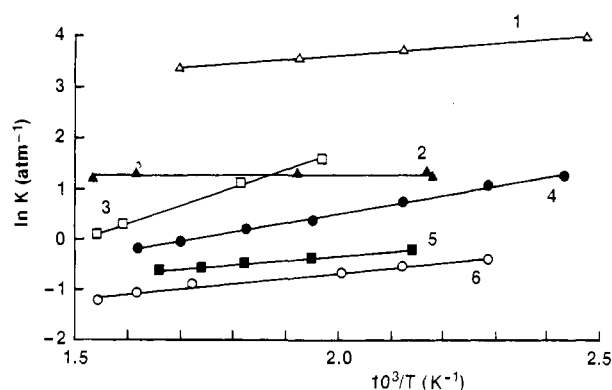


Figure 1. van't Hoff plots for charge-transfer and proton-transfer equilibria for the reactants as follows: (1) DMT<sup>+</sup> + Cp<sub>2</sub>Fe; (2) DET<sup>+</sup> + Cp<sub>2</sub>Fe; (3) Cp<sub>2</sub>FeH<sup>+</sup> + 3-Fpyridine; (4) Cp<sub>2</sub>FeH<sup>+</sup> + 2-Fpyridine; (5) Cp<sub>2</sub>FeH<sup>+</sup> + 1,4-diazine; (6) Cp<sub>2</sub>FeH<sup>+</sup> + pyrrole.

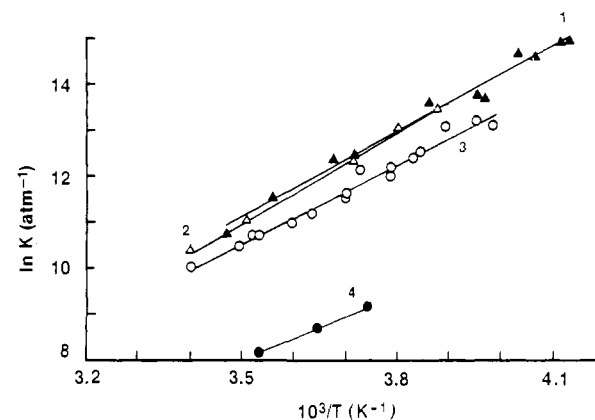


Figure 2. van't Hoff plots for clustering reactions: (1) Cp<sub>2</sub>Fe<sup>+</sup> + *N,N*-dimethyl-4-toluidine; (2) Cp<sub>2</sub>FeH<sup>+</sup> + CH<sub>3</sub>CN; (3) Cp<sub>2</sub>Fe<sup>+</sup> + CH<sub>3</sub>CN; (4) Cp<sub>2</sub>Fe<sup>+</sup>·CH<sub>3</sub>CN + CH<sub>3</sub>CN.

tainty of the reference IPs, the present results for the IP of Cp<sub>2</sub>Fe may be given as 6.81 with an expected error of 0.07 eV (157.1 ± 1.6 kcal/mol).

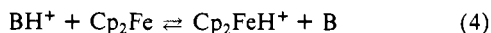
In comparison, the ionization potential has been measured by electron ionization as 6.7–6.9 eV.<sup>3,4</sup> More recently, a value of 6.717 eV was obtained by Bar et al., by photoelectron spectroscopy.<sup>11</sup> However, this value included an estimated correction of 420 cm<sup>-1</sup> due to a tail attributed to the ionization of hot molecules.

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Our value is in the middle of the range of the literature values and is in good agreement within the combined error limits.

**2. Proton Affinity.** The proton affinity of  $\text{Cp}_2\text{Fe}$  was measured by proton-transfer equilibria with reference compounds B. Several equilibria were measured as a function of temperature.



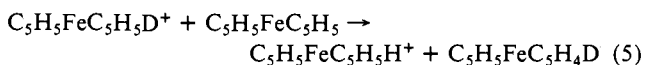
$\Delta G^\circ_4$  gives the gas-phase basicity and  $\Delta H^\circ_4$  the proton affinity of  $\text{Cp}_2\text{Fe}$  relative to the reference compound B. The results are summarized in Table I. From  $\Delta H^\circ_4$  with the four reference bases, the proton affinity of  $\text{Cp}_2\text{Fe}$  is determined as  $207.0 \pm 1$  kcal/mol. We note that pyrrole as a reference compound gives a PA value lower by about 1 kcal/mol than the other reference bases. This may suggest that the literature value of PA(pyrrole) is too low by about 1 kcal/mol.

The results also show a significant entropy change upon the protonation of  $\text{Cp}_2\text{Fe}$ . After accounting for  $\Delta S^\circ_{\text{rot sym}}$  for  $\text{BH}^+ \rightarrow \text{B} = -1.4$  cal/mol·K for the reference compounds 1,4-diazine and pyrrole, the first three reference compounds give the entropy change for  $\text{Cp}_2\text{Fe} \rightarrow \text{Cp}_2\text{FeH}^+$  as  $+6.3 \pm 1$  cal/mol·K. Reaction 6 in Table I gives a somewhat higher value, possibly due to experimental error. We note that the overall molecular rotational symmetry number of  $\text{Cp}_2\text{Fe}$  is 10, and elimination of this symmetry could contribute  $\Delta S^\circ = 4.6$  cal/mol·K. Structural implications of the entropy change will be discussed below.

The present value of  $\text{PA}(\text{Cp}_2\text{Fe}) = 207.0$  kcal/mol is somewhat lower than the results of Foster and Beauchamp,<sup>12</sup> which, taking into account the current evaluated PAs of their reference compounds, is  $210 \pm 4$  kcal/mol. The difference is due in part to the entropy of protonation of  $\text{Cp}_2\text{Fe}$ , which was not accounted for in the single-temperature bracketing measurements. Considering the entropy effect brings the present and bracketing values within better than 2 kcal/mol.

From the present IP and PA values, the homolytic bond dissociation energy  $\Delta H^\circ_{\text{D}}(\text{Cp}_2\text{Fe}^+-\text{H})$  is calculated as  $50 \pm 2$  kcal/mol. This is lower than the value given by Foster and Beauchamp,  $56 \pm 6$  kcal/mol,<sup>12</sup> since they used both higher PA and IP values. As noted by these authors, the homolytic bond dissociation energy is substantially lower than the homolytic bond dissociation energies in most organic and inorganic compounds, which range between 80 and 130 kcal/mol, but it is in the range of typical M-H homolytic bond dissociation energies, which are around 60 kcal/mol.

**3. Site of Protonation.** Protonation of ferrocene occurs on the iron atom in solution<sup>16</sup> and presumably also in the gas phase.<sup>12</sup> We tested this by deuteration experiments as follows. A mixture of 5%  $\text{D}_2\text{O}$  in  $\text{N}_2$  was used as reactant gas, with 0.08%  $\text{Cp}_2\text{Fe}$  added. Under these conditions the major reactant ion is  $\text{D}_3\text{O}^+$ , which rapidly transfers  $\text{D}^+$  to ferrocene. The only observed product was  $\text{Cp}_2\text{FeD}^+$ , and  $\text{Cp}_2\text{FeH}^+$  was not observed up to 2-ms reaction time. During this time,  $\text{Cp}_2\text{FeD}^+$  undergoes about 50 collisions with  $\text{Cp}_2\text{Fe}$ . If the incoming  $\text{D}^+$  was on a ring carbon, thermoneutral hydrogen exchange between equivalent ring hydrogens in the ionic and neutral collision partners would be expected, as such reactions are common and fast in most gas-phase bases.<sup>17,18</sup> Because of the large excess of hydrogens, deuteration would be lost in the exchange process



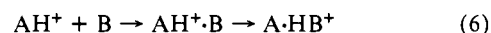
For thermoneutral proton exchange, the collision efficiency would be expected to be 0.1–1, and significant production of the  $\text{Cp}_2\text{FeH}^+$  would be expected, in analogy to H/D exchange in benzene derivatives.<sup>17</sup> In comparison, the efficiency of reaction 5 is less than 0.02. The absence of this process here indicates that the incoming  $\text{D}^+$  goes to an energetically favored unique site and does not exchange with ring hydrogens.

A unique protonation site was also confirmed by a protonation–deprotonation experiment. In this experiment the carrier gas was 18%  $\text{D}_2\text{O}$  in  $\text{CH}_4$ . Here,  $\text{D}_3\text{O}^+$  reacts to produce  $\text{Cp}_2\text{FeD}^+$ , and ions originating from  $\text{CH}_4$  produce some  $\text{Cp}_2\text{FeH}^+$ . Subsequently, these ions react with a proton acceptor, 2-Me-pyridine, that was added in small concentration. Under our conditions the fast initial chemical ionization processes produced  $\text{Cp}_2\text{FeD}^+$  and  $\text{Cp}_2\text{FeH}^+$  in the ratio of about 80:20. These ions reacted and produced 2-Me-pyridine $\text{D}^+$  and 2-Me-pyridine $\text{H}^+$  in a similar ratio, 80:20. This again shows that in the deprotonation of  $\text{Cp}_2\text{FeD}^+$  the incoming deuteron was lost without scrambling. In comparison, proton transfer after complete scrambling of hydrogens from a  $\text{C}_5\text{H}_5\text{D}$  ring of  $\text{Cp}_2\text{FeD}^+$  would have produced, considering the original 2-methylpyridine $\text{H}^+$  present, the products 2-Me-pyridine $\text{D}^+$  and 2-Me-pyridine $\text{H}^+$  in the ratio 13:87. Scrambling between H and D on the deuterated ring carbon atom would have produced a 2-Me-pyridine $\text{D}^+$  to 2-Me-pyridine $\text{H}^+$  ratio of 40:60. Neither is consistent with the 80:20 excess of 2-Me-pyridine $\text{D}^+$  to 2-Me-pyridine $\text{H}^+$  as observed. Therefore, this experiment also confirms that the incoming deuteron or proton attaches at a unique site, retains its identity, and is then lost upon deprotonation.

The results are consistent with protonation on iron or the formation of an agostic  $\text{Fe}-\text{H}^+-\text{ring}$  structure. Protonation on iron would decrease  $\sigma_{\text{rot sym}}$  (considering overall rotations and internal  $\sigma_{\text{rot sym}} = 5$  from the rotation of one ring vs the other) from 50 to 10 and account for  $\Delta S^\circ_{\text{rot sym}}$  of  $+R \ln 5 = 3.2$  cal/mol·K. The agostic structure, still allowing an internal 5-fold rotation, would lead to  $\Delta S^\circ_{\text{rot sym}} = R \ln 10 = 4.6$  cal/mol·K.

Similar results, with a unique non-scrambling protonation–deprotonation site and in  $\Delta S^\circ_{\text{rot sym}} = R \ln 5$  would be produced by ring protonation in a sterically favored exo position. However, this is unlikely, especially with the deuterating agent being the small  $\text{D}_3\text{O}^+$  ion and the deuteron transfer being exothermic by 40 kcal/mol, which is probably more than sufficient to overcome the endo–exo energy difference.

The absence of the self-exchange reaction 5 can also give an estimate for the difference between the protonation energies on iron and on the ring. For this, it is assumed that ring protonation would result in reaction 5 with ultimate loss of deuterium and, also, that deuteron transfer from the iron of  $\text{Cp}_2\text{FeD}^+$  to the ring of the neutral  $\text{Cp}_2\text{Fe}$  in a collision complex would ultimately result in loss of deuteration. Experience with other compounds shows that H/D exchange occurs if the overall process (6), including proton transfer within the complex, is exothermic.<sup>17,18</sup>



Assuming that the hydrogen-bonded  $\text{Cp}_2\text{H}^+\cdot\text{Cp}_2\text{Fe}$  dimer is bonded by at least 5 kcal/mol (a conservative, low value for ionic hydrogen bonding) would make (6) exothermic and H/D transfer possible, if iron-to-ring proton transfer was endothermic by less than 5 kcal/mol. The observed absence of H/D exchange therefore suggests that iron-to-ring proton transfer in ferrocene is endothermic by at least 5 kcal/mol.

In conclusion, the deuteration experiments show that ferrocene is protonated at an energetically favored, stereochemically unique site. This site may be directly on iron, or an agostic iron– $\text{H}^+$ –ring structure, or exo protonation on a ring. The thermochemistry is consistent with protonation on iron, both in the entropy change and in the value of  $D(\text{Cp}_2\text{Fe}^+-\text{H}) = 50 \pm 2$  kcal/mol, which is similar to  $D(\text{Fe}^+-\text{H}) = 49 \pm 1.5$  kcal/mol.<sup>19</sup> Furthermore, photoionization spectra suggest that the  $e_{2g}$  SOMO of  $\text{Cp}_2\text{Fe}^+$  originates about 65% from the Fe 3d orbital<sup>11</sup> and 35% from the ring. Therefore, the SOMO is concentrated mostly on iron, which would indicate that protonation should also occur on that site in the gas phase, as well as it does in solution. However, since part of the SOMO is on the rings, this argument also allows for an agostic structure. Our data are consistent with the general evidence for protonation on iron but cannot rule out other energetically favored unique geometries for the incoming proton such

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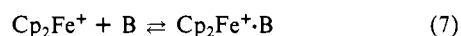
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as an agostic or ring exo protonation.

**4. Interaction with Solvent Molecules.** Solvation plays an important role in electrode reactions and electron-transfer reactions involving the  $\text{Cp}_2\text{Fe}^+$  radical cation. The interaction energies with solvent molecules are obtained from clustering equilibria (7).



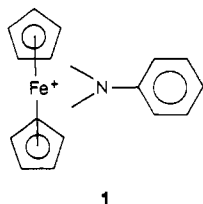
The results are summarized in Table I. In comparison with the bonding energies of gas-phase ions to highly polar solvent molecules such as  $\text{CH}_3\text{CN}$ , which range up to 30 kcal/mol,<sup>2</sup>  $\text{Cp}_2\text{Fe}^+$  is one of the most weakly solvated ions measured. For example, the interaction energy of 11.4 kcal/mol may be compared with  $\Delta H^\circ_{\text{D}}$  for  $\text{K}^+\cdot\text{CH}_3\text{CN}$  and  $\text{NH}_4^+\cdot\text{CH}_3\text{CN}$ , which are over 20 kcal/mol.<sup>2</sup>

The bonding energy of  $\text{Cp}_2\text{Fe}^+\cdot\text{CH}_3\text{CN}$  to the second solvent molecule is, as usual, somewhat reduced, 9.1 kcal/mol. The interaction of  $\text{Cp}_2\text{Fe}^+$  with  $\text{CH}_3\text{CN}$  molecules is probably mostly electrostatic, and the weak bonding is due to the delocalization of the charge in the large ion.

Attempts to measure clustering equilibria with several other solvents were not successful. The problem was that the bonding is weak and equilibria would require low ion-source temperatures, but ferrocene was observed to condense out in the ion source below  $-40^\circ\text{C}$ . The limiting values showed the interaction energy with  $(\text{CH}_3)_2\text{O}$  is  $<8.7$  kcal/mol. This is in accordance with the difference of bonding energies of  $\text{CH}_3\text{CN}$  and  $(\text{CH}_3)_2\text{O}$  to several ions, where the former is usually stronger by 2–4 kcal/mol.

We investigated recently<sup>19,20</sup> bonding in homonuclear aromatic dimer cations such as bis(benzene)<sup>+</sup>, bis(aniline)<sup>+</sup>, and bis(*N,N*-dimethyl-4-toluidine)<sup>+</sup> ( $\text{DMT}_2^+$ ). These dimers can form charge-transfer complexes with a sandwich geometry, and most of the homonuclear dimers are bonded by 16–18 kcal/mol. In comparison, in bis(ferrocene)<sup>+</sup> the bonding is weaker than 13 kcal/mol. Evidently, the  $\pi$  system, being bonded to  $\text{Fe}^+$ , is an inefficient donor for intermolecular charge-transfer complexing, and iron-to-iron bonding may be sterically hindered. No significant interaction of  $\text{Cp}_2\text{Fe}^+$  with benzene as a donor is observed either.

However, a complex could be observed with the stronger electron donor DMT. Recent calculations suggest that the nitrogen lone pair is the favored electron donor in this molecule, and the structure of the complex may be as in ion 1.



1

In this complex the IPs of the components are similar. The bonding strengths in aromatic charge-transfer complexes demonstrated that this facilitates charge-transfer resonance contributions of up to 5 kcal/mol in the dimer ions. However, the bonding energy of 12.2 kcal/mol in  $\text{Cp}_2\text{Fe}^+\text{-DMT}$  is fairly weak, compared, for example, with  $\Delta H^\circ(\text{DMT}_2^+) = 16.9$  kcal/mol. This may be due to diminished dispersion forces in ion 1 compared with the sandwich-type aromatic dimers.

We also measured the interaction energy of the protonated species  $\text{Cp}_2\text{FeH}^+$  with  $\text{CH}_3\text{CN}$ . The interaction energy is similar to that of the radical cation, again quite weak for a  $\text{BH}^+\text{-NCCCH}_3$  hydrogen bond. For comparison, ammonia and methylamine have PAs comparable to  $\text{Cp}_2\text{Fe}$ , but  $\Delta H^\circ_{\text{D}}$  for  $\text{NH}_4^+\cdot\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{NH}_3^+\cdot\text{CH}_3\text{CN}$  is larger than that for  $\text{Cp}_2\text{FeH}^+$  by more than 5 kcal/mol. Assuming protonation on iron, this shows that the  $\text{-FeH}^+$  moiety is not an efficient hydrogen bond donor.

In conclusion, the interactions of  $\text{Cp}_2\text{Fe}^+$  and  $\text{Cp}_2\text{FeH}^+$  with solvent molecules are weak. These large, charge-delocalized

**Table II.** Rate Constants for Charge-Transfer and Proton-Transfer Reactions

B <sup>+</sup> or BH <sup>+</sup>	T, K	k <sup>a</sup>	$\Delta H^\circ$ <sup>b</sup>	$\Delta S^\circ$	$\Delta G^\circ$ <sup>b</sup>
Charge-Transfer Reactions B <sup>+</sup> + C <sub>2</sub> Fe → Cp <sub>2</sub> Fe <sup>+</sup> + B					
DMT <sup>+</sup>	583	16	-1.8	1.0	-4.2
	429	17	-1.8	1.0	-3.6
DET <sup>+</sup>	618	13	-0.1	2.2	-1.5
	461	12	-0.1	2.2	-1.1
Proton-Transfer Reactions BH <sup>+</sup> + Cp <sub>2</sub> Fe → Cp <sub>2</sub> FeH <sup>+</sup> + B					
C <sub>6</sub> H <sub>7</sub> <sup>+</sup>	615	22	-40.5	2.8	-42.2
CH <sub>3</sub> CNH <sup>+</sup>	601	19	-18.6	6.3	-22.4
C <sub>2</sub> H <sub>5</sub> CNH <sup>+</sup>	637	18	-14.4	6.3	-18.2
<i>i</i> -C <sub>3</sub> H <sub>7</sub> CNH <sup>+</sup>	620	17	-12.7	6.3	-16.5
NH <sub>4</sub> <sup>+</sup>	629	26	-3.0	9.4	-8.6
2-methylthiopheneH <sup>+</sup>	585	1.7	-1.3	6.3	-4.8
	515	1.5	-1.3	6.3	-4.5
pyrroleH <sup>+</sup>	621	0.15	+2.2	5.6	-1.2
	541	0.16	+2.2	5.6	-0.8
1,4-diazineH <sup>+</sup>	602	0.42	+1.8	4.2	-0.8
	513	0.49	+1.8	4.2	-0.3
2-PyridineH <sup>+</sup>	615	1.5	+3.6	6.2	-0.2
	588	1.4	+3.6	6.2	-0.1
Proton-Transfer Reactions Cp <sub>2</sub> FeH <sup>+</sup> + B → BH <sup>+</sup> + Cp <sub>2</sub> Fe					
3-Pyridine	577	4.1	-7.3	-6.3	-0.8
<i>i</i> -C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub>	547	3.5	-11.6	-8.5	-7.6
<i>t</i> -C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub>	591	7.1	-13.8	-8.5	-8.8
pyridine	541	4.0	-13.8	-6.3	-10.4

<sup>a</sup> Units of  $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . Estimated error  $\pm 50\%$ . <sup>b</sup>  $\Delta H^\circ$  and  $\Delta G^\circ$  in kcal/mol,  $\Delta S^\circ$  in cal/mol·K.  $\Delta H^\circ$  from present results of ref 2, 14, and 15.  $\Delta S^\circ$  from present results or with 6.3 cal/mol·K for the protonation of  $\text{Cp}_2\text{Fe}$  and  $R \ln \sigma_{\text{rot, sym}}$  for the protonation of the reference compounds (both overall and internal rotational symmetry changes considered).

**Table III.** Rate Constants of Proton-Transfer and Ligand-Switching Reactions

B <sub>2</sub> H <sup>+</sup>	T, K	k <sup>a</sup>	$\Delta H^\circ$ <sup>b</sup>	$\Delta S^\circ$ <sup>b</sup>	$\Delta G^\circ$ <sup>b</sup>
Proton Transfer B <sub>2</sub> H <sup>+</sup> + Cp <sub>2</sub> Fe → C <sub>2</sub> FeH <sup>+</sup> + 2B					
(CH <sub>3</sub> CN) <sub>2</sub> H <sup>+</sup>	471	1.7	11.2	31.0	-3.4
	298	1.1	11.2	31.0	+2.0
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CNH <sup>+</sup>	508	2.2	15.6	31.9	-0.6
	384	0.6	15.6	31.9	+3.4
Ligand Switching B <sub>2</sub> N <sup>+</sup> + Cp <sub>2</sub> Fe → Cp <sub>2</sub> FeH <sup>+</sup> ·B + B					
(CH <sub>3</sub> CN) <sub>2</sub> H <sup>+</sup>	471	1.7	-0.2	12.1	-5.9
	298	1.1	-0.2	12.1	-3.8
(C <sub>2</sub> H <sub>5</sub> CN) <sub>2</sub> H <sup>+</sup>	508	2.2	3.6	11.9	-2.4
	384	0.6	3.6	11.9	-0.7

<sup>a</sup> Units of  $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . Error estimate  $\pm 50\%$ . <sup>b</sup>  $\Delta H^\circ$  and  $\Delta G^\circ$  in kcal/mol,  $\Delta S^\circ$  in cal/mol·K. Thermochemistry from present data and from estimates based on  $\Delta H^\circ_{\text{D}}$  vs  $\Delta \text{PA}$  correlations.<sup>30</sup>

cations interact with neutral molecules more weakly than most other cations.

**5. Kinetics of Charge-Transfer and Proton-Transfer Reactions.** In the course of the charge-transfer and proton-transfer equilibrium measurements, kinetic data were obtained from approach to equilibrium.

The charge-transfer reactions in Table II proceed near unit collision efficiency. This is usual for exothermic charge-transfer reactions, although reactions exothermic by less than 1 kcal/mol often slow down to 0.5–0.2 of the collision rate. However, this slowing is not observed here even for nearly thermoneutral charge transfer from DET<sup>+</sup>.

Proton-transfer reactions to  $\text{Cp}_2\text{Fe}$  that are both exothermic ( $\Delta H^\circ < 0$ ) and exergonic ( $\Delta G^\circ < 0$ ) also proceed at about unit efficiency. However, several exergonic proton-transfer reactions in Table II proceed at rates of  $1\text{--}4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , significantly below unit efficiency.

Several of the slow reactions in Table II are endothermic but, because of the positive entropy of protonation of  $\text{Cp}_2\text{Fe}$ , are still exergonic. The thermochemistry is similar to reactions observed previously where conformational or rotational entropy changes rendered  $\Delta G^\circ$  negative.<sup>21–23</sup> In all cases, the exergonic reactions,

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even when endothermic by up to 7 kcal/mol, proceeded near unit efficiency. These were termed entropy-driven reactions. Therefore, the endothermic nature of the present slow exergonic reactions is not sufficient to explain the slow rate.

Exergonic proton-transfer reactions of cations observed to date were slow only in sterically hindered systems, such as alkylpyridines,<sup>24</sup> and in C<sub>3</sub>-C<sub>5</sub> trialkylamines at elevated temperatures.<sup>25</sup> These reactions always display large negative temperature coefficients.

In the present case most of the slow reactions occur when  $\Delta G^\circ$  is only slightly negative and/or the reactants are cyclic compounds such as (2-methylthiophene)H<sup>+</sup>, (pyrrole)H<sup>+</sup>, (1,4-diazine)H<sup>+</sup>, (2-Fpyridine)H<sup>+</sup>. The reactions are somewhat slower than collision rate even when proton transfer occurs from Cp<sub>2</sub>Fe to pyridine, a substantially exothermic as well as exergonic reaction. If Cp<sub>2</sub>Fe is protonated on iron, there could be steric hindrance to the approach of the cyclic moieties to the iron. In addition, if optimal approach between the proton donor and acceptor sites in the transfer reaction is prevented, this could result in an energy barrier, as theoretical work by Scheiner has shown.<sup>26</sup> This could also lead to slow kinetics.

According to transition-state theory, steric hindrance in the transition state, leading to the freezing of free rotors in the transition state, would result in negative temperature coefficients,<sup>27</sup> which are not observed. On the other hand, an energy barrier would result in a positive temperature coefficient, which is also not observed.

Experimentally, as shown in Table II, the reactions do not exhibit a significant temperature coefficient of either sign over the narrow temperature range of the present experiments. Similar combinations of slow kinetics with small temperature coefficients were observed previously in charge-transfer<sup>28</sup> and methyl cation transfer<sup>29</sup> reactions, which involve substantial energy barriers. Specifically, in those reactions the energy barrier is similar to the bonding energy in (AH<sup>+</sup>·B), so that the potential energy of the transition state is near that of the reactants. As we saw above, the hydrogen bonding of Cp<sub>2</sub>FeH<sup>+</sup> in ionic complexes is weak, probably <8 kcal/mol for the present reactants. Therefore, energy barriers of 4–8 kcal/mol could explain the observed kinetics. It is also possible that the kinetic behavior observed here is due to a combination of an energy barrier and steric effects, which result in opposing and canceling temperature dependencies.

In summary, several proton-transfer reactions to and from ferrocene exhibit slow kinetics with small or negligible temperature coefficients. These are the first proton-transfer reactions observed to exhibit such a behavior. It may be due to the combination of an energy barrier and steric hindrance, both associated with a protonation site on metal, which is inaccessible for optimal approach to the reaction partners. Such a situation could be common to organometallic compounds. The kinetics of proton transfer in organometallic systems will therefore be of interest.

**6. Proton Transfer from Cluster Ions.** Table II shows kinetic data obtained for proton transfer from several protonated dimer cations to Cp<sub>2</sub>Fe. The interesting feature is that the reactions proceed at significant rates, although below unit efficiency, even though endothermic by up to 18 kcal/mol. However, these re-

actions involve large positive entropy changes because of cluster dissociation. Therefore,  $\Delta G^\circ$  is negative at high temperatures.

The energy barrier to these reactions must be at least equal to  $\Delta H^\circ$ . The enthalpy factor  $\Delta H^\circ/RT$  would slow the cluster ion reactions in Table II by 10<sup>-5</sup>–10<sup>-9</sup>. However, the collision efficiencies are much larger, from 0.1 to 0.001, due to the positive entropy changes. The term "entropy-driven" has been applied to fast ion-molecule reactions. The present, somewhat slower reactions may be termed "entropy-enhanced".

Entropy-driven reactions of cluster ions were observed in anionic organometallic systems, such as the reactions of OH<sup>-</sup>·*n*H<sub>2</sub>O and CH<sub>3</sub>O<sup>-</sup>·*n*CH<sub>3</sub>OH (*n* = 3 and 4) with Fe(CO)<sub>5</sub>.<sup>31</sup> However, it was pointed out that rather than being a one-step entropy-driven process the reaction may involve ligand switching followed by cluster dissociation.<sup>31,32</sup> Applied to the present systems, the alternatives are reaction 8, or 9 followed by 10.

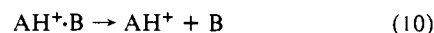
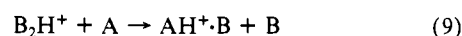
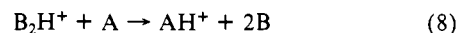


Table III shows that, for A = Cp<sub>2</sub>Fe and B = CH<sub>3</sub>CN, both reactions 8 and 9 are exergonic at high temperatures. However, at the lower observed temperature,  $\Delta G^\circ_8$  becomes positive, while  $\Delta G^\circ_9$  is still negative, and therefore ligand switching may be favored. Similar relations apply for B = C<sub>2</sub>H<sub>5</sub>CN. However, an interesting observation here is that both reactions 8 and 9 are endothermic. Therefore, whether dissociative transfer or ligand switching occurs, the actual exergonic channel is endothermic and entropy-enhanced.

### Summary

This work is the first comprehensive pulsed mass spectrometric study of a transition-metal organometallic compound. The results give accurate equilibrium IP and PA values and further decrease the previously noted low  $\Delta H^\circ_{\text{D}}(\text{Cp}_2\text{Fe}^+-\text{H})$  bond energy. The thermochemistry and deuteration results are consistent with a unique protonation site, possibly an agostic bridged structure. The results also show some features that are unusual in gas-phase ion chemistry. These include the following: very low solvation energies; slow proton transfer with small or no temperature coefficient, possibly indicative of an energy barrier combined with steric hindrance; and entropy-driven proton transfer from cluster ions.

The unique features are associated with a metal being the protonation site and with steric hindrance to the access to the metal. These features are common to organometallics. Therefore, this class of compounds promises to show interesting ion-molecule reaction kinetics.

**Acknowledgment.** I thank Dr. D. Richardson for a sample of purified ferrocene and Drs. D. Richardson and J. F. Liebman for helpful discussions. This work was supported in part by a grant from the Office of Basic Research, U.S. Department of Energy.

**Note Added in Proof.** Recently, Kebarle and co-workers measured the protonation thermochemistry of ferrocene in good agreement with the present values. They also observed slow proton transfer kinetics, and on kinetic basis concluded that Cp<sub>2</sub>FeH<sup>+</sup> binds weakly to neutrals and that ring protonation is weaker by 210 kcal/mol than protonation of iron. These results are complementary to and consistent with the present measurements. (Ikonomou, M. G.; Sunner, J.; Kebarle, P. *J. Phys. Chem.* **1988**, *92*, 6308.)

**Registry No.** DMT, 99-97-8; DET, 613-48-9; Cp<sub>2</sub>Fe, 102-54-5; Cp<sub>2</sub>Fe<sup>+</sup>, 12125-80-3; Cp<sub>2</sub>FeH<sup>+</sup>, 86527-04-0; CH<sub>3</sub>CN, 75-05-8; (CH<sub>3</sub>)<sub>2</sub>O, 115-10-6; C<sub>6</sub>H<sub>6</sub>, 71-43-2; *i*-C<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>, 75-31-0; *i*-C<sub>4</sub>H<sub>9</sub>NH<sub>2</sub>, 75-64-9; (CH<sub>3</sub>CN)<sub>2</sub>H<sup>+</sup>, 85559-51-9; (C<sub>2</sub>H<sub>5</sub>CN)<sub>2</sub>H<sup>+</sup>, 118298-96-7; pyrrole, 118298-96-7; 1,4-diazine, 290-37-9; 2-fluoropyridine, 372-48-5; 3-fluoropyridine, 372-47-4; pyridine, 110-86-1.

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