

ording to eq 32, within relatively narrow limits. Proton transfer from protonated dimethyl carbonate to $\text{Fe}(\text{CO})_5$ is readily observed, but no proton transfer is seen from NH_4^+ . This is interpreted to mean that $\text{PA}[(\text{CH}_3\text{O})_2\text{CO}] \leq \text{PA}[\text{Fe}(\text{CO})_5] \leq \text{PA}[\text{NH}_3]$. Recent results from our laboratory indicate that $\text{PA}[(\text{CH}_3\text{O})_2\text{CO}] = 203 \pm 2$ kcal/mol,³⁰ and thus $\text{PA}[\text{Fe}(\text{CO})_5]$ is assigned as 204 ± 3 kcal/mol. Iron pentacarbonyl is thus actually quite a strong base in the gas phase. The difference in gas phase and solution behavior is attributable to the understandably poor solvation of $\text{HFe}(\text{CO})_5^+$.

The decomposition of $\text{HFe}(\text{CO})_5^+$ by loss of CO is observed when it is formed in a sufficiently exothermic proton transfer reaction. This reaction is observed with all proton donors less basic than dimethyl ether. These results indicate that $D[\text{HFe}(\text{CO})_4^+ - \text{CO}] = 23 \pm 10$ kcal/mol, which is not significantly different from the CO binding energy in the parent ion (22 kcal/mol).

Conclusions

The results described above indicate that ICR has tremendous potential for illuminating certain aspects of organometallic chemistry. It is to be stressed that such experiments are performed at low pressure in the gas phase and provide information relating to the intrinsic reactivity of the molecules studied in the absence of solvent effects. The results above suggest that aspects of particular interest may be: (1) formation of polynuclear metal clusters containing varying numbers and types of ligands, (2) ligand substitution processes, (3) determination of relative ligand binding energies, (4) accurate determination of transition metal basicity, (5) characterization of processes involving both electrophilic and nucleophilic attack on neutral metal complexes, (6) generation and study of unusual σ - and π -bonded organometallic complexes, and (7) photochemistry of gaseous organometallic ions.³¹

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Ion-Molecule Reactions and Gas-Phase Basicity of Ferrocene

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Abstract: The gas-phase ion chemistry of ferrocene is investigated using the techniques of ion cyclotron resonance spectroscopy. Product distributions and rate constants for the principal primary ions are determined using trapped ion methods. Proton transfer reactions in mixtures of ferrocene with other molecules place fairly accurate limits on the gas-phase basicity of the molecule, leading to a proton affinity (213 ± 4 kcal/mol) which is slightly less than methylamine. The gas-phase measurements are free from complicating solvent effects which have previously led to some unwarranted conclusions about transition-metal basicity.

The unusual structures and bonding of dicyclopentadienyl metal complexes (metallocenes) have stimulated many mass spectral investigations of these molecules.^{2,3} Of particular interest is the recent high-pressure study of ferrocene

by Schildcrout,⁴ who demonstrated the occurrence of several ion-molecule reactions. The present paper describes an ion cyclotron resonance (ICR) study of the ion chemistry of ferrocene, both alone and in mixtures with several other

molecules. This investigation continues our efforts to apply the powerful ICR technique to transition-metal organometallic species.⁵ Ferrocene is a logical choice for examination because of its high stability, adequate vapor pressure, and position as the most chemically significant metallocene.

In addition to elucidating the reactions of the ions derived from ferrocene, these experiments place fairly accurate limits on the gas-phase basicity of the molecule. The latter information is particularly significant in view of the mechanism invoked for electrophilic substitution in the metallocenes.⁶ It is to be emphasized that the experiments described are performed at low pressure in the gas phase, in the absence of complicating solvent effects which have apparently led to some unwarranted conclusions about transition-metal basicity.

Experimental Section

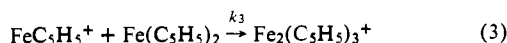
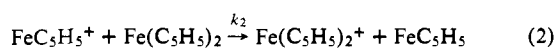
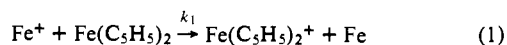
The general features and operating characteristics of ICR instrumentation have been previously described in detail.⁷ Equipped with a "flat" cell modified for trapped-ion operation,⁸ the spectrometer used in the present study was constructed at Caltech and is capable of improved resolution over a wider mass range (upper limit $\sim m/e$ 600) than previously available instruments. The pulse circuitry which permits both trapped-ion and normal drift-mode operation will be detailed elsewhere.⁹

Ferrocene was obtained from Aldrich Chemical Co. and used as supplied; no impurities were evident in the ICR mass spectrum. The vapor pressure of ferrocene at room temperature is about 10^{-2} Torr,¹⁰ which was adequate for all of the present experiments when the vapor from a crystalline sample was introduced by means of the normal inlet system (i.e., through a variable leak valve). Heating the sample was not required. All experiments were performed at ambient temperature (25–30°). Accurate pressure measurements were made with a Schulz-Phelps type ion gauge calibrated against a MKS Baratron Model 90H1-E capacitance manometer in the manner previously described.¹¹ The estimated uncertainty in absolute pressures, and thus in all rate constants reported, is $\pm 10\%$. Ferrocene was extremely well-behaved in the ICR spectrometer and no experimental difficulties were encountered.

Results and Discussion

Ion Chemistry of Ferrocene. The 70 eV ICR mass spectrum of ferrocene at 1.0×10^{-7} Torr agrees with previous electron impact results.² The ions observed and their relative abundances are: $\text{Fe}(\text{C}_5\text{H}_5)_2^+$ (100), FeC_5H_5^+ (48), and Fe^+ (16). The parent ion was most prominent at all electron energies.

At an electron energy of 70 eV, one ion-molecule reaction product appears at m/e 307 as the pressure of ferrocene is raised. At a pressure of 7×10^{-5} Torr, Fe^+ and FeC_5H_5^+ have disappeared in favor of the parent ion and the product ion at m/e 307. Double resonance experiments⁷ unambiguously identify the charge-exchange reactions, eq 1 and 2, and the condensation reaction, eq 3, as occurring in this sys-



tem, the latter being responsible for the product at m/e 307, which presumably has a "triple-decker sandwich" structure.⁴ The parent ion appears unreactive, a conclusion verified by lowering the electron energy to 11 eV, which is below the appearance potentials of Fe^+ and FeC_5H_5^+ ,^{3a} and noting that no reaction products occur out to m/e 500. Processes 1–3 are the same as those deduced by Schildcrout from high-pressure mass spectrometry experiments.⁴ With no neutral product, process 3 is unusual for an ion-molecule

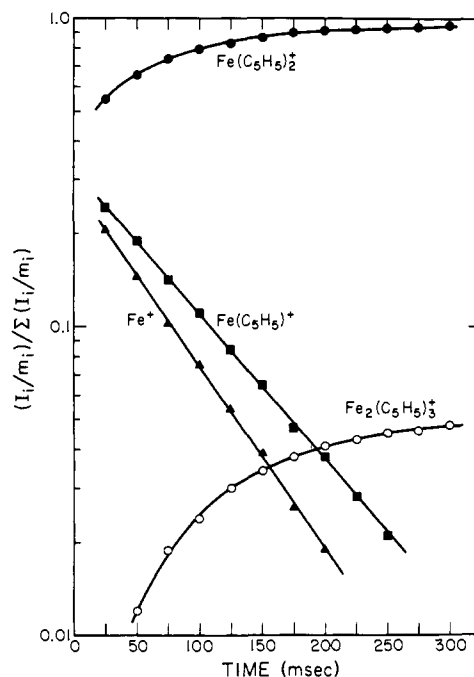


Figure 1. Variation with time of positive ion abundances in ferrocene following a 10 msec, 70 eV electron beam pulse at a pressure of 4.3×10^{-7} Torr. I_i and m_i represent the ICR single resonance intensity and mass of the i th ionic species. The quantity I_i/m_i is proportional to ion abundance.

reaction occurring at fairly low pressure, but several other examples of this behavior have been noted recently.^{12,13} No protonated ferrocene is observed in pure $\text{Fe}(\text{C}_5\text{H}_5)_2$, a result discussed further below.

Recently developed ICR trapped-ion techniques⁸ were applied to this system to accurately determine the rate constants of reactions 1–3. The variation with time of the four ions observed in ferrocene following a 10 msec, 70 eV electron beam pulse is shown in Figure 1. As expected from the reaction scheme, the Fe^+ and FeC_5H_5^+ ion intensities decay exponentially with time. From the slopes of the lines in Figure 1 and the known pressure, rate constants for the disappearance of Fe^+ and FeC_5H_5^+ are determined to be $9.8 \pm 1.0 \times 10^{-10}$ and $7.9 \pm 0.8 \times 10^{-10}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. The former is identified with k_1 and the latter with $k_2 + k_3$. The exponential rise of $\text{Fe}_2(\text{C}_5\text{H}_5)_3^+$ (see Figure 1) provides an independent determination of k_3 , which is measured as $1.2 \pm 0.1 \times 10^{-10}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. Subtracting this from the total rate for disappearance of FeC_5H_5^+ gives $k_2 = 6.7 \pm 0.7 \times 10^{-10}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

Table I lists the ion-molecule reactions occurring in ferrocene along with the rate constants measured in this work, those reported by Schildcrout,⁴ and those predicted by the Langevin polarization theory.¹⁴ The absolute rates determined by high-pressure mass spectrometry are about three times those determined by ICR, a rather poor agreement between the two very different techniques. However, the ratios between the two sets of data are constant within experimental error (k/k_S in Table I). Correspondingly, the relative rate constants in each set of data are also identical within experimental error. The discrepancy between the two sets of rate determinations can thus be attributed entirely to uncertainties in the absolute pressure. The indirect pressure measurement technique used by Schildcrout⁴ involves an ionization gauge far removed from the source region of the mass spectrometer and at 10^4 lower pressure. As he points out, the method is subject to considerable uncertainty. The

Table I. Ion-Molecule Reactions and Rate Constants^a in Ferrocene

Reaction	k^b	k_S^c	k/k_S	k_L^d
$\text{Fe}^+ + \text{Fe}(\text{C}_5\text{H}_5)_2 \rightarrow \text{Fe}(\text{C}_5\text{H}_5)_2^+ + \text{Fe}$	0.98 ± 0.10	2.6 ± 0.5	0.38 ± 0.11	1.55
$\text{FeC}_5\text{H}_5^+ + \text{Fe}(\text{C}_5\text{H}_5)_2 \rightarrow \text{Fe}(\text{C}_5\text{H}_5)_2^+ + \text{FeC}_5\text{H}_5$	0.67 ± 0.07	2.1 ± 0.7	0.32 ± 0.14	1.19
$\text{FeC}_5\text{H}_5^+ + \text{Fe}(\text{C}_5\text{H}_5)_2 \rightarrow \text{Fe}_2(\text{C}_5\text{H}_5)_3^+$	0.12 ± 0.01	0.34 ± 0.12	0.35 ± 0.16	

^a All rate constants in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. ^b This work. ^c Reference 4. ^d Langevin polarization theory rate; see ref 14. The molecular polarizability of ferrocene is given as $18.9 \times 10^{-24} \text{ cm}^3$ in Ya. G. Dorfman, *Russ. J. Phys. Chem. (Engl. Transl.)*, 37, 1347 (1963).

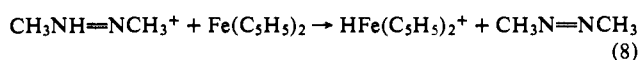
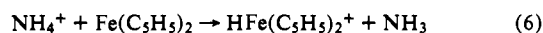
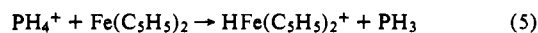
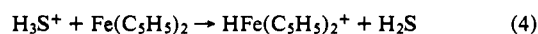
Table II. Proton Transfer Reactions Involving Ferrocene

Reaction observed ^a	Thermochemical inference ^b
$\text{H}_2\text{S}^+ + \text{Fe}(\text{C}_5\text{H}_5)_2 \rightarrow \text{HFe}(\text{C}_5\text{H}_5)_2^+ + \text{H}_2\text{S}$	$\text{PA}[\text{Fe}(\text{C}_5\text{H}_5)_2] \geq 170^c$
$\text{PH}_4^+ + \text{Fe}(\text{C}_5\text{H}_5)_2 \rightarrow \text{HFe}(\text{C}_5\text{H}_5)_2^+ + \text{PH}_3$	$\text{PA}[\text{Fe}(\text{C}_5\text{H}_5)_2] \geq 188^d$
$\text{NH}_4^+ + \text{Fe}(\text{C}_5\text{H}_5)_2 \rightarrow \text{HFe}(\text{C}_5\text{H}_5)_2^+ + \text{NH}_3$	$\text{PA}[\text{Fe}(\text{C}_5\text{H}_5)_2] \geq 207^e$
$(i\text{-Pr})_2\text{OH}^+ + \text{Fe}(\text{C}_5\text{H}_5)_2 \rightarrow \text{HFe}(\text{C}_5\text{H}_5)_2^+ + (i\text{-Pr})_2\text{O}$	$\text{PA}[\text{Fe}(\text{C}_5\text{H}_5)_2] \geq 208^e$
$\text{CH}_3\text{NH}=\text{NH}_3^+ + \text{Fe}(\text{C}_5\text{H}_5)_2 \rightarrow \text{HFe}(\text{C}_5\text{H}_5)_2^+ + \text{CH}_3\text{N}=\text{NCH}_3$	$\text{PA}[\text{Fe}(\text{C}_5\text{H}_5)_2] \geq 209^f$
$\text{HFe}(\text{C}_5\text{H}_5)_2^+ + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NH}_3^+ + \text{Fe}(\text{C}_5\text{H}_5)_2$	$\text{PA}[\text{Fe}(\text{C}_5\text{H}_5)_2] \leq 216^g$

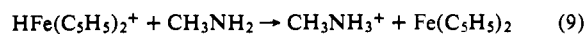
^a dK/dE negative in each case. Reverse reaction not observed. ^b Values in kcal/mol. PA = proton affinity, defined in text. ^c M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, 73, 4328 (1969). ^d Reference 12. ^e M. Taagepera and R. W. Taft, unpublished results. ^f M. S. Foster and J. L. Beauchamp, *Int. J. Mass Spectrom. Ion Phys.*, 15, 429 (1974). ^g Reference 23.

direct method used in the present ICR experiments has proven highly accurate in previous work and is expected to yield absolute pressures to within $\pm 10\%$ in this situation. The total ICR reaction rates for Fe^+ and FeC_5H_5^+ are about two-thirds of those predicted by the Langevin formulation. Those of Schildcrout are a factor of 2 higher. Rarely do measured rate constants exceed the Langevin rate in nonpolar systems.

Basicity of Ferrocene. Mixtures of ferrocene with select molecules were examined to delineate the nature of proton transfer reactions occurring in these systems. Molecules examined included H_2S , PH_3 , NH_3 , $(i\text{-Pr})_2\text{O}$, $\text{CH}_3\text{N}=\text{NCH}_3$, and CH_3NH_2 . Proton transfer reactions 4–8, confirmed in each case by double resonance, were observed in binary mixtures of ferrocene with the respective neutral molecule. In a mixture of $\text{Fe}(\text{C}_5\text{H}_5)_2$ with a large



excess of CH_3NH_2 , no protonated ferrocene is observed although CH_3NH_3^+ is the dominant ion present. But in a 2:1:2 mixture of $\text{Fe}(\text{C}_5\text{H}_5)_2$, CH_3NH_2 , and H_2S , reaction 4 occurs readily and is followed by reaction 9 in which $\text{HFe}(\text{C}_5\text{H}_5)_2^+$ transfers a proton to CH_3NH_2 . The proton



affinity of a molecule M, $\text{PA}(\text{M})$, is defined as the enthalpy change for the gas-phase reaction $\text{MH}^+ \rightarrow \text{M} + \text{H}^+$ and represents a quantitative measure of intrinsic basicity.^{7,15} Thermochemical data relevant to reactions 4–9 are presented in Table II, from which the proton affinity of ferrocene is established as $213 \pm 4 \text{ kcal/mol}$, corresponding to $\Delta H_f^\circ[\text{HFe}(\text{C}_5\text{H}_5)_2^+] = 205 \pm 5 \text{ kcal/mol}$.¹⁶

The molecular orbital in ferrocene from which the lowest energy ionization process occurs is the e_{2g} orbital, localized largely on the iron atom and consisting of the metal d_{xy} and $d_{x^2-y^2}$ electrons.^{3c} Presumably, protonation of ferrocene also involves this orbital, which is consistent with the well-accepted observation that ferrocene protonates in solution on the metal atom.^{17–19} Protonation only occurs in the presence of strong acids, however, suggesting a relatively low

basicity for ferrocene in solution.^{17,20} This has been interpreted as reflecting the rather nonspecific diffuse iron localized nature of the e_{2g} orbital.^{19,20} In contrast, the gas-phase results show ferrocene to be surprisingly basic, with a proton affinity higher than that of ammonia (eq 6). The metal-based electrons in ferrocene thus have substantial donor capabilities, consistent with the proposal that the metal atom is the site of attack in electrophilic substitution reactions.^{2,6} A similar conclusion is appropriate in the case of iron pentacarbonyl, whose proton affinity has recently been measured as $204 \pm 3 \text{ kcal/mol}$.²¹ This molecule also protonates on the metal atom in solution.²² The significantly higher basicity of $\text{Fe}(\text{C}_5\text{H}_5)_2$ relative to $\text{Fe}(\text{CO})_5$ may reflect the fact that the metal d electrons in the latter are more involved in retrodonative π bonding to the CO groups and thus reduce the electron donor ability of the metal relative to ferrocene. The tremendous difference observed between the solution and gas-phase basicity of ferrocene probably reflects the understandably poor solvation of the protonated molecule.

The homolytic bond dissociation energy $D(\text{M}^+-\text{H})$, defined as the enthalpy change for the reaction $\text{MH}^+ \rightarrow \text{M}^+ + \text{H}$, is related to the proton affinity of M by eq 10. This

$$\text{PA}(\text{M}) - D(\text{M}^+-\text{H}) = \text{IP}(\text{H}) - \text{IP}(\text{M}) \quad (10)$$

dissociation energy is useful in correlating gas phase basicities because it is generally constant for a homologous series of molecules, leading to a linear relationship between $\text{PA}(\text{M})$ and $\text{IP}(\text{M})$.^{7,23} From the ionization potential of ferrocene ($6.8 \pm 0.1 \text{ eV}$),^{2a} $D[\text{H}-\text{Fe}(\text{C}_5\text{H}_5)_2^+]$ is calculated to be $56 \pm 6 \text{ kcal/mol}$. This number is extraordinarily low compared with those for other organic and inorganic molecules (which generally range between 80 and 130 kcal/mol)⁷ and accounts for the absence of $\text{HFe}(\text{C}_5\text{H}_5)_2^+$ with ferrocene alone in the gas phase. The analogous bond energy in $\text{HFe}(\text{CO})_5^+$ is calculated to be $74 \pm 3 \text{ kcal/mol}$,²⁴ still low by comparison with other molecules but substantially higher than that in ferrocene. Not surprisingly, $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{C}_5\text{H}_5)_2$ cannot be considered two members of a homologous series from the standpoint of (M^+-H) bond energies.

It is found in all molecules studied to date that (M^+-H) bond energies are greater than $(\text{M}-\text{H})$ bond energies in the corresponding isoelectronic neutral molecule [e.g., $D(\text{PH}_3^+-\text{H}) > D(\text{SiH}_3-\text{H})$].^{7,25} Such a situation may obtain for transition metal-hydrogen bonds as well; the $(\text{Mn}-\text{H})$ bond energy in $\text{HMn}(\text{CO})_5$ is low, certainly less than 74 kcal/mol .²⁶ In view of the already weak $[\text{H}-$

$\text{Fe}(\text{C}_5\text{H}_5)_2^+$ bond, that in $\text{HMn}(\text{C}_5\text{H}_5)_2$ may be especially so, perhaps accounting for the fact that the latter species has never been observed while its Tc and Re analogs are well-known. The extension of these results to other organometallic complexes, containing a variety of metal atoms and ligands, should prove illuminating.

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Photochemical and Photophysical Processes in Acetophenone

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Abstract: Besides the first-order radiative ($1.2 \times 10^2 \text{ sec}^{-1}$) and radiationless ($5.3 \times 10^2 \text{ sec}^{-1}$) decay channels the lifetime and emission yield of gaseous triplet acetophenone depends upon (a) diffusion to followed by quenching at the wall, (b) self-quenching ($8.9 \times 10^7 M^{-1} \text{ sec}^{-1}$), and (c) photoreaction. The contribution of diffusion can be treated quantitatively and it is shown that the wall deactivates with close to unit efficiency. At sufficiently low pressure following $S_0 \rightarrow S_2$ excitation, triplet acetophenone dissociates with unit probability to give $\text{C}_6\text{H}_5\text{CO}\cdot + \text{CH}_3\cdot$. The dissociative state can be deactivated by added gas and both emission and chemical quantum yields give a dissociative lifetime of $\sim 5 \times 10^{-8}$ sec for $\lambda_{\text{excit}} 275$ nm. There is evidence that these lifetimes are wavelength sensitive. $S_0 \rightarrow S_1$ excitation does not result in the above reaction although there is evidence for a temperature-dependent decay.

In a previous paper we discussed the photochemistry of benzaldehyde,¹ and in this paper we report on our studies of acetophenone.² Benzaldehyde photochemistry is very sensitive to the energy of excitation and on the nature of the electronic state excited. For example $S_0 \rightarrow S_1$ excitation ($n \rightarrow \pi^*$) resulted in free radical formation; $S_0 \rightarrow S_2$ excitation ($\pi \rightarrow \pi^*$) led to an intramolecular process resulting in benzene and CO without the formation of free radicals. The triplet yield was somewhat wavelength dependent, and it has been suggested that the rate of intersystem crossing decreases with an increase in excitation wavelength.³ Thus we were particularly interested to determine the nature of and the relative importance of the primary photochemical processes in gaseous acetophenone as a function of excitation energy. Furthermore a knowledge of these primary photochemical processes was necessary before studying the bimolecular reactions of triplet acetophenone in the gas phase. The results of these latter studies will be reported in another paper.⁴

Early studies^{5,6} of the photolysis of acetophenone were directed to the search for a convenient source of phenyl rad-

icals in the gas phase. Both methyl and phenyl radicals were produced in sufficient quantity for rate studies when photolyses using an unfiltered mercury arc were carried out at elevated temperatures ($>280^\circ$).⁶ Carbon monoxide, benzene, ethane, methane, and trace amounts of biphenyl and toluene were produced under these conditions. The use of acetophenone as a radical source in the glass was also attempted.⁷ However, full mercury arc irradiation of acetophenone in a 5:1 isopentane-3-methylpentane glass at liquid nitrogen temperature resulted in no detectable decomposition.

The above mentioned studies reveal little about the nature of the primary photochemical processes involved since unfiltered light was used. Smith and Calvert⁸ studied the $S_0 \rightarrow S_1$ photolysis of trifluoroacetophenone at 366 and 313 nm at elevated temperatures (150-300°). They concluded the quantum yield for decomposition was extremely small, under their conditions: for example, at 366 nm and 280°, $\Phi_{\text{CF}_3} \sim 0.008$.

Experimental Section

- (1) **Materials and Apparatus.** Acetophenone was distilled on a