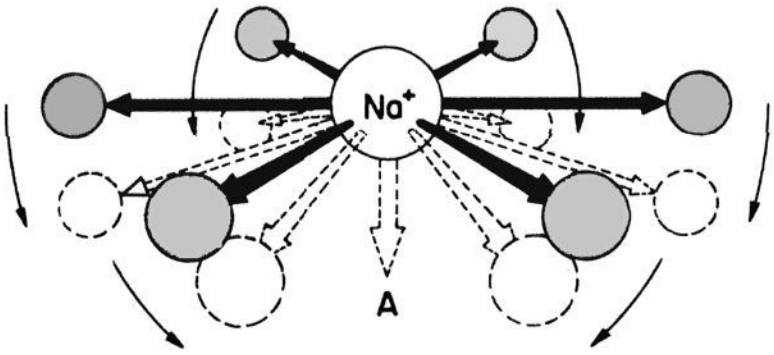

Figure 4.

DBC complexes may reflect the greater flexibility of the macrocyclic ring in DCC.

Absolute values of the rate constants of decomplexation at $-13°$, determined for 0.3 M solutions of the sodium salt, are given in column 7 of Table III. The comparison of different systems based on such relatively diluted solutions is significant, since for the ionic strength <0.3 the apparent rate constants seem to approach their limiting values.

Extrapolation of these values based on the experimentally determined E_a and reported in the literature equilibrium constants yields values of k_{-2} and k_2 at 25°, listed in the last two columns of Table III. As one may expect, the rate constants of complexation increase with the increase in the stability of the complexes, while the rate constants of decomplexation are shifted in the opposite direction. A direct determination of the rate constant of complexation of sodium ions with DBC in methanol at 25° was attempted by Chock and Funck[13] who used the ultrasonic relaxation technique for the investigation of this system. They found $k_2^{25°} = 6 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. The agreement between this value and our extrapolated value of $k_2^{25°} \approx 3.2 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ may be regarded as very satisfactory, especially since the two values were arrived at by completely different experimental techniques.

Acknowledgment. We thank Professor Z. Luz for helpful suggestions.

High-Pressure Mass Spectra and Gaseous Ion Chemistry of Ferrocene

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Abstract: Electron-impact mass spectra of ferrocene have been obtained at 70 eV with ion-source pressures up to 1.5×10^{-2} Torr at 400°K. Ion–neutral reactions observed are those of Fe^+ and $FeC_5H_5^+$ with ferrocene, with rate constants of $(2.6 \pm 0.5) \times 10^{-9}$ and $(2.4 \pm 0.5) \times 10^{-9}$ cm^3 molecule^{-1} sec^{-1}, respectively, at a nominal repeller field of 4.6 V cm^{-1}. Reaction of $FeC_5H_5^+$ with ferrocene gives rise to charge transfer in competition with the formation of the stable adduct $Fe_2(C_5H_5)_3^+$. This adduct contributes up to 3% of the total ion current and is formed with a rate constant of $(3.4 \pm 1.2) \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}.

The investigation of gaseous ion–neutral reactions, or ion chemistry, has so far emphasized organic and very simple inorganic systems. The extension of this field of study to include as many classes of compounds as possible should aid the understanding of this type of reaction. An important class of compounds whose ion chemistry has been subjected to little previous study is that of transition metal complexes.[1] There appear to be no reports of measurements of rate constants for reaction of ions with a transition metal complex.

Ferrocene, or di-π-cyclopentadienyliron(II), $Fe(C_5H_5)_2$, is an appropriate choice for a study of ion–neutral reactions by mass spectrometry since it is a relatively simple complex, its bonding properties are of interest, it has an appreciable vapor pressure, and its vapor has high thermal stability. Metallocenes including ferrocene have been subjects of mass spectrometric studies, which have been recently reviewed.[2,3]

The ion $Fe_2(C_5H_5)_3^+$ at m/e 307 has been reported with an abundance of 0.06% of the total ion current in the mass spectrum of ferrocene at an ion-source pressure of 10^{-5} Torr. This ion was presumed to be a product of ion–neutral reaction and to have a "triple-decker sandwich" structure,[4] although no concrete evidence for either of these suppositions was given. It has since been suggested that it may arise in the mass spectrum by fragmentation of a small amount of neutral ferrocene dimer, rather than from ion–neutral reaction.[5]

The present work was undertaken to determine the feasibility of an ion–neutral reaction study of a transition metal complex by single-source electron-impact mass spectrometry, to determine the reactions occurring between ferrocene and its positive fragment ions and the rates of these reactions, and to

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(1) (a) M. S. Foster and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **93**, 4924 (1971); (b) J. Müller and K. Fenderl, *Chem. Ber.*, **103**, 3141 (1970); *ibid.*, **104**, 2199, 2207 (1971).

(2) G. A. Junk and H. J. Svec in "Recent Topics in Mass Spectrometry," R. I. Reed, Ed., Gordon and Breach, New York, N. Y., 1971, p 85.

(3) M. Cais and M. S. Lupin, *Advan. Organometal. Chem.*, **8**, 211 (1970).

(4) E. Schumacher and R. Taubenest, *Helv. Chim. Acta*, **47**, 1525 (1964).

(5) R. W. Kiser in "Characterization of Organometallic Compounds," Part I, M. Tsutsui, Ed., Interscience, New York, N. Y., 1969, p 137.

obtain evidence indicating the origin of $Fe_2(C_5H_5)_3^+$ in the ferrocene mass spectrum.

Experimental Section

Ferrocene, CP (Research Organic/Inorganic Chemical Corp.), was used without further purification. The mass spectrum showed no interfering impurities.

Mass spectra were obtained with a CEC (Du Pont) 21-491 double-focusing mass spectrometer. This instrument has a "closed" ion source with differential pumping on the ion-source and analyzer regions. Unless otherwise indicated, the ionizing energy was 70 eV, the ion-repeller potential was 2.2 V giving a field of 4.6 V cm^{-1}, and the ion-source temperature was 400°K, which should not cause significant thermal decomposition of ferrocene.[6] Ferrocene was introduced *via* a direct probe inlet, which was heated between 330 and 400°K to produce the desired pressure in the ion source.

Pressure in the ion source was determined by monitoring an ionization gauge on the analyzer region. The ratio of pressure in the ion source to that at the gauge was established by observing the reaction of O^+ with CO_2, whose rate constant is taken as 1.2×10^{-9} cm^3 $molecule^{-1}$ sec^{-1}.[7] This ratio is found to be 7.5×10^3 for CO_2 over the range of pressures considered. Since both CO_2 and ferrocene should be pumped efficiently by the mass spectrometer's liquid nitrogen traps, the pressure of ferrocene in the ion source is taken as 7.5×10^3 times that in the analyzer region as for CO_2.

Ionization gauge readings were corrected to allow for the different ionization cross sections of air, carbon dioxide,[8] and ferrocene. The molecular ionization cross section of ferrocene is estimated to be 38×10^{-16} cm^2 by two methods. One method considers the diamagnetic susceptibility[9] and the empirical correlation between susceptibility and ionization cross section reported by Beran and Kevan.[10] The other assumes additivity of atomic and molecular cross sections and uses the cross sections of cyclopentane[8] and Fe and H atoms.[11] Although both methods are expected to yield only approximate results, their agreement in the case of ferrocene seems to justify the use of this value.

Results and Discussion

Using the CO_2 calibration procedure described above it was found that ion-source pressures as high as 1.5×10^{-2} Torr of ferrocene could be achieved.

Scanning the mass spectrum of ferrocene to *m/e* ~650 at the various pressures showed significant abundances of the primary (formed by dissociative ionization) ions Fe^+ and $FeC_5H_5^+$, what will be shown to be a secondary (formed by ion–neutral reaction) ion $Fe_2(C_5H_5)_3^+$, and the parent ion $Fe(C_5H_5)_2^+$ which is also produced to some extent by a secondary process. This parent ion is the most abundant ion at all pressures studied. The four ionic species to be considered were identified by their masses and isotope ratios. No readily measurable abundances of other species containing more than one iron atom were found. Minor fragments such as $C_5H_5^+$ constituted less than 1% of the total ionization and are not considered further.

Primary Ions. The relative abundances of Fe^+ and $FeC_5H_5^+$ are shown as functions of *N*, the concentration of ferrocene molecules in the ion source, in Figure 1. The linear decrease in the logarithm of the relative abundance of these ions as ferrocene concentration increases is evidence of a bimolecular, pseudo-first-order reaction of the ion with ferrocene.

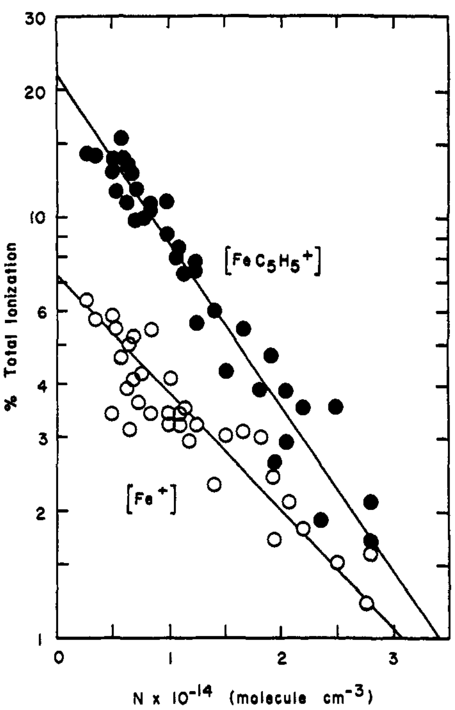

Figure 1. Relative abundances of Fe^+ and $FeC_5H_5^+$ *vs.* ferrocene concentration. The ion-source temperature is 400°K, the ion-repeller potential is 2.2 V, and the ionizing energy is 70 eV.

The rate constants are calculated from the slopes of the lines as previously described.[7] In this method the available reaction time is taken as the time for free flight of the reactant ion through the reaction region in the field of the ion repeller. This is valid when the mean free path of the ion is not much smaller than the distance it must travel to leave the ion source, as in the case of the pressures used here.

The ionic product of these reactions is considered to be mainly $Fe(C_5H_5)_2^+$, formed by charge transfer

$$Fe^+ + Fe(C_5H_5)_2 \longrightarrow Fe + Fe(C_5H_5)_2^+ \qquad (1)$$

and

$$FeC_5H_5^+ + Fe(C_5H_5)_2 \longrightarrow FeC_5H_5 + Fe(C_5H_5)_2^+ \qquad (2)$$

Since the ionization potential of the iron atom[12] is greater than that of ferrocene[13-15] by slightly less than 1 eV, (1) is energetically allowed. The exothermicity of (2) cannot be calculated this way since the ionization potential of FeC_5H_5 is not known. At low pressures $Fe(C_5H_5)_2^+$ constitutes about 70% of the total ionization. At higher pressure this contribution increases by more than would be expected from (1) alone. This indicates that the products of (2) are correctly given. As will be shown below the reaction

$$FeC_5H_5^+ + Fe(C_5H_5)_2 \longrightarrow Fe_2(C_5H_5)_3^+ \qquad (3)$$

competes with (2).

From the decrease in Fe^+ abundance (Figure 1) the rate constant for (1) is calculated as $k_1 = (2.6 \pm$

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[7] S. M. Schildcrout and J. L. Franklin, *J. Chem. Phys.*, 51, 4055 (1969).

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[15] A. Foffani, S. Pignataro, G. Distefano, and G. Innorta, *ibid.*, 7, 473 (1967).

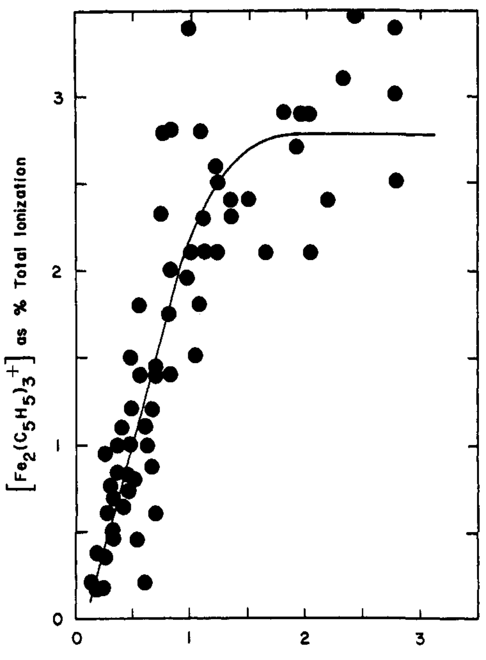

Figure 2. Relative abundance of $Fe_2(C_5H_5)_3^+$ *vs.* ferrocene concentration. The ion-source temperature is 400°K, the ion-repeller potential is 2.2 V, and the ionizing energy is 70 eV.

0.5) × 10^{-9} cm^3 $molecule^{-1}$ sec^{-1}. Similarly the total rate constant for loss of $FeC_5H_5^+$ is $k_2 + k_3 = (2.4 \pm 0.5) \times 10^{-9}$ cm^3 $molecule^{-1}$ sec^{-1}. Determination of k_3 (see below) permits evaluation of $k_2 = (2.1 \pm 0.7) \times 10^{-9}$ cm^3 $molecule^{-1}$ sec^{-1}. These rate constants are about twice as great as those typically found for fast ion–neutral reactions involving small molecules.

Secondary Ions. Besides the $Fe(C_5H_5)_2^+$ formed by (1) and (2) the only other secondary ion of importance in these experiments is $Fe_2(C_5H_5)_3^+$. Its relative abundance as a function of ferrocene concentration is shown in Figure 2. The abundance achieves a constant value of 3% of the total ionization at the higher ferrocene pressures. This is a 50-fold increase over the amount observed at lower pressure by Schumacher and Taubenest.[4] It would seem unlikely that this much $Fe_2(C_5H_5)_3^+$ could be formed from a neutral ferrocene dimer[5] which has apparently escaped previous detection.

Experiments at various ion-repeller potentials were carried out at $N = 7.5 \times 10^{13}$ molecules cm^{-3}. While it was not possible to establish a reliable quantitative relationship, the data in Figure 3 show that the relative $Fe_2(C_5H_5)_3^+$ abundance decreases as the potential on the repeller increases, *i.e.*, as ion-residence time in the reaction region decreases. This behavior is typical for secondary ions. If this ion were a primary ion from ferrocene dimer, its relative abundance should either increase or remain constant depending on whether it reacted further with ferrocene or not.

The data in Figure 2 were obtained while the ionizing electron current, as measured from the total ion current produced, was varied over a factor of 3. The agreement among these data indicates that $Fe_2(C_5H_5)_3^+$ originates in a process involving only one reactant electron, which forms the primary ion. Thus the neutral reactant must be ground-state ferrocene rather than a free radical or electronically excited species.

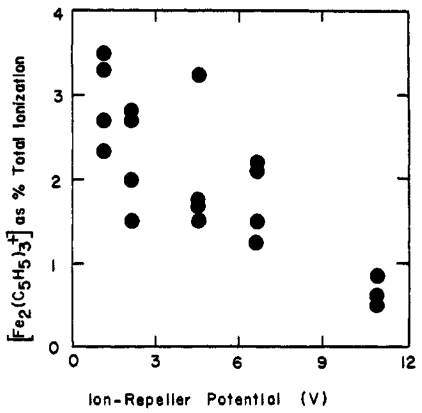

Figure 3. Relative abundance of $Fe_2(C_5H_5)_3^+$ *vs.* ion-repeller potential. The ion-source temperature is 400°K, the ferrocene concentration is 7.5 × 10^{13} molecules cm^{-3}, and the ionizing energy is 70 eV.

Schumacher and Taubenest[4] suggested that $Fe_2(C_5H_5)_3^+$ is formed by reaction 3 since they found its appearance potential to be the same as that of $FeC_5H_5^+$. A rough check of appearance potentials now confirms their observation.

All of the present data are consistent with $Fe_2(C_5H_5)_3^+$ being formed predominately, if not exclusively, by (3) under the conditions of these experiments. This ion has been reported also by King[16] as a primary fragment in the mass spectrum of $(C_5H_5FeCO)_4$, where it was found to undergo further fragmentation *via* a metastable process

$$Fe_2(C_5H_5)_3^+ \longrightarrow Fe(C_5H_5)_2^+ + FeC_5H_5 \qquad (4)$$

The observation of these products rather than neutral ferrocene and $FeC_5H_5^+$ is evidence that FeC_5H_5 has a higher ionization potential than ferrocene. The charge transfer (2) would then be exothermic and a likely reaction in the present system. Since the modes of formation of $Fe_2(C_5H_5)_3^+$ in King's experiment and in the present case are different, its average energy and hence the rate of (4) in each case may be quite different. There is no evidence that (4) occurs at a significant rate in the present system.

Supposing that the abundance of $Fe_2(C_5H_5)_3^+$ in ferrocene is determined by the rates of (2) and (3), the expression

$$[Fe_2(C_5H_5)_3^+] = \frac{k_3}{k_2 + k_3}[FeC_5H_5^+]_0(1 - e^{-(k_2+k_3)tN} \qquad (5)$$

is derived where $[Fe_2(C_5H_5)_3^+]$ is the relative abundance of $Fe_2(C_5H_5)_3^+$, $[FeC_5H_5^+]_0$ is the relative abundance of $FeC_5H_5^+$ extrapolated to $N = 0$, and t is the time available for reaction of $FeC_5H_5^+$ in the ion source. At small values of N the slope of the curve in Figure 2 is then

$$\Delta[Fe_2(C_5H_5)_3^+]/\Delta N = k_3t[FeC_5H_5^+]_0 \qquad (6)$$

and at large values of N the limiting value of $[Fe_2(C_5H_5)_3^+]$ is

$$[Fe_2(C_5H_5)_3^+]_{max} = \frac{k_3}{k_2 + k_3}[FeC_5H_5^+]_0 \qquad (7)$$

Since $k_2 + k_3$ has been determined, the data of Figure 2

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[16] R. B. King, *Org. Mass Spectrom.*, 2, 657 (1969).

may be used with either (6) or (7) to obtain $k_3 = (3.4 \pm 1.2) \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}.

Conclusions

Ferrocene is amenable to study in the ion source of a mass spectrometer at pressures up to 1.5×10^{-2} Torr. The fragment ions Fe^+ and $FeC_5H_5^+$ both undergo rapid charge transfer with neutral ferrocene. These reactions are exothermic for ground-state reactants.

The binuclear adduct $Fe_2(C_5H_5)_3^+$ is formed from reaction of $FeC_5H_5^+$ and ferrocene and does not undergo further reaction under the present conditions. Charge transfer involving $FeC_5H_5^+$ occurs about six times as fast as the competing adduct formation. The rate constants for reaction of Fe^+ and $FeC_5H_5^+$ with ferrocene are about twice those predicted by the polarization theory of Gioumousis and Stevenson,[17] using the relationship

$$k = 2\pi e\sqrt{\alpha/\mu} \tag{8}$$

where e is the charge on the ion, α is the molecular polarizability of ferrocene,[9] and μ is the reduced mass of the reacting system. Considering the limitations of the theory,[18] the agreement is good and perhaps fortuitous, but it suggests no significant steric or energetic barrier to these reactions.

Further studies of gaseous ion chemistry of metal complexes should provide useful information about reactions and chemical species not occurring or not easily studied in condensed or neutral systems.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Low-Temperature Chemical Ionization Mass Spectrometry of Boron Hydrides. The Proton Affinities of Diborane and Tetraborane(10)

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Abstract: Low-temperature chemical ionization spectra of B_2H_6, B_4H_{10}, and B_5H_9 in methane have been obtained. Protonation of B_2H_6 to yield $B_2H_7^+$ is observed in CH_4 between 79 and 86°K. The proton affinity of B_2H_6 is determined to be 147 ± 4 kcal/mol. In the B_2H_6–CH_4 and B_2H_6–H_2 systems $B_4H_{11}^+$ is formed by addition of $B_2H_5^+$ to B_2H_6 between 80 and 140°K and between 80 and 115°K, respectively. From the observed heat of formation of $B_4H_{11}^+$, the proton affinity of B_4H_{10} is calculated to be 144 ± 5 kcal/mol. For the B_4H_{10}–CH_4 and B_5H_9–CH_4 systems ion interconversions are studied as a function of temperature. These results indicate the relative ordering of the zero point energies of several $B_4H_n^+$ and $B_5H_n^+$ ions.

In a recent publication[1] we reported the results of a chemical ionization study of the common boron hydrides with a number of ionizing reagents. These results showed that B_5H_9 and B_6H_{10} are moderately strong bases. Independently, Johnson, *et al.*,[2] have isolated the $B_6H_{11}^+$ cation in a strong acid medium. Chemical ionization of B_2H_6, B_4H_{10}, and B_5H_{11} by CH_5^+ at source temperatures of 100–200° leads to hydride abstraction from the boron hydride with the formation of $(M - 1)^+$ ions. Only an estimate of the proton affinity of diborane could be obtained from these measurements. It is possible that failure to detect the $(M + 1)^+$ ion in these experiments was due to thermodynamic instability of the ion at the operating source temperature or to complicated kinetic factors in the proton transfer mechanism. To examine these problems further we have modified our experimental technique for study of these processes at low temperatures. The results of this investigation have led to a better understanding of the nature of the proton transfer process in these systems and have provided information on the proton affinities of B_2H_6 and B_4H_{10}.

Experimental Section

The design of the low-temperature chemical ionization (CI) source used in this study is illustrated in Figure 1. The ion box and inlet tube were constructed of 304 stainless steel. Source pressures were measured with a McLeod gauge through a side-arm connection into the source cavity. An ion repeller was located 1.2 cm from the ion exit hole. For most experiments the source field strength was maintained at either 10 or 23 V/cm (in this range of field strengths the extent of chemical ionization was seen to vary but not the essential processes of interest). Rhenium filaments were used, and the electron accelerating energy was fixed at 300 V. The source was sandwiched between two heavy copper blocks fitted with refrigeration coils. With liquid nitrogen as coolant it was possible to attain source temperatures between 79 and 310°K (the ambient temperature with hot filament). Temperatures were measured with a chromel-alumel thermocouple spot-welded to the source. The thermocouple voltage was monitored continuously on a Varian Model No. G-2010 recorder. The source pressure was controlled by adjusting the inlet gas flow rate with a Nupro

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