Properties and Reactions of Some Inorganic and Organometallic Compounds in the Gas Phase

Thesis by

Michael Stewart Foster

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To my parents,

whose love and encouragement over the years
is at least as responsible as my own efforts
for producing this thesis.

Acknowledgments

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Abstract

The gas-phase ion-molecule reactions occurring in several inorganic and organometallic systems have been examined by ion cyclotron resonance (icr) spectroscopy.

Electron attachment to sulfur hexafluoride under collision-free conditions has been shown to produce stable SF_6^- by a radiative de-excitation process. Halide ion transfer reactions involving anions derived from several covalent sulfur halides produce the hydrogen dihalide anions, XHY^- (X, Y = halogen), and other interesting anionic dimers. These results have important implications for radiolysis experiments which employ SF_6 as an electron scavenger.

The ion-molecule reactions of iron pentacarbonyl are characterized by the formation of polynuclear clusters containing up to four iron atoms. Extensive carbon monoxide replacement reactions are also observed with a wide variety of σ- and π-bonding ligands. $Fe(CO)_5$ is shown to have a proton affinity slightly less than that of ammonia.

The fragment ions derived from ferrocene undergo charge exchange with the parent neutral and condense with it to form $Fe_2(C_5H_5)_3^+$. The proton affinity of ferrocene is very high, the molecule being only slightly less basic than methylamine. Some general conclusions are reached about the concept of transition metal basicity.

The proton affinity of hydrogen fluoride has been determined as 1 kcal/mole less than that of nitrogen. The anomalous behavior of HF relative to the other hydrogen halides is discussed.

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CHAPTER 1

Introduction

Ionic species are ubiquitous in nature and processes involving ions as reactants or products have always been a subject of significant chemical interest. The chemistry of ions rather naturally divides itself in two general areas: ions in solution and ions in gases. The former has been the more traditional area of investigation, to which attest, for example, the extensive bodies of knowledge of analytical chemistry and electrochemistry. In contrast, meaningful laboratory studies of the reactions of gaseous ions are relatively recent, beginning only about twenty years ago. This is primarily due to the necessity of employing rather sophisticated techniques to generate, maintain, and study ions in the gas phase. It has become apparent, however, that the effort required to carry out such studies is well rewarded by the insight gained into the fundamental behavior and chemical reactivity of the systems considered.

The impetus for studying gas-phase reactions between ions and molecules derives from several sources. Ion-molecule reactions are important in the chemistry of flames, arcs and discharges, shock waves, radiolysis systems, planetary atmospheres, and interstellar space. Studying such systems in the laboratory requires application of the modern techniques of ion chemistry. In addition, many ions can be produced and studied in the gas phase which could never exist in solution because of their highly reactive nature. More importantly, the chemical behavior of ions which do exist in solution is strongly modified by the presence of the solvent. The reactivity of ions in the condensed phase reflects the nature of the ion-solvent system and not simply the nature of the ion; many situations have been documented in which the solvent totally obscures the fundamental chemical behavior of the ion. On the other hand, by studying the same reaction in solution and in the gas phase, detailed information can be obtained about the influence of solvent on chemical properties and reactivity, information that is generally impossible to obtain otherwise. Specific examples of many of the considerations mentioned above are discussed in this thesis.

The first recognized example of an ion-molecule reaction occurring in the gas phase dates from the early days of conventional mass spectrometry. Dempster[1] in 1916 observed an ion of mass three in the spectrum of hydrogen, which he attributed to the process

$$H_2^+ + H_2 \rightarrow H_3^+ + H \quad .$$

Several other simple ion-molecule reactions were observed subsequently, but significant interest in the field only developed after the reaction

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$$

was reported by Tal'roze and Lyubimova in 1952.[2] Concurrent with the availability of improved equipment and vacuum technology, this burgeoning interest has grown dramatically and resulted in an exponential growth of publications in the field.[3] Quite a number of sophisticated techniques have been developed to study ion-molecule processes,[4] one of the most versatile and successful being ion cyclotron resonance spectroscopy (icr).

The theory, instrumentation, and applications of icr have been described in detail in the literature.[5] Several salient features of the technique, however, are worth emphasizing here. Ions are produced in an icr spectrometer by electron impact on a gaseous sample, as in a more conventional mass spectrometer. The ions are formed in a strong magnetic field, which constrains their motion to a circular orbit (typical radius = 0.02 cm) and contains them within the relatively small icr cell (1.25 x 2.5 x 13 cm). As the ions move in well-defined trajectories through the cell, collisions with gas molecules provide the opportunity for ion-molecule reactions. In the normal drift-mode icr experiment, the residence time of the ion in the cell (~ 1 msec) is kept constant and the pressure is varied to control the number of collisions experienced. Within the usual experimental pressure range of 10^{-5} to 10^{-3} mm of Hg, the number of collisions per ion will be 1 - 100. In the trapped-ion mode of operation, the pressure is kept constant while the residence time of the ion in the cell is varied, typically between 10 and 1000 msec. At the usual pressure of 10^{-6} mm of Hg, each ion will again suffer 1 - 100 collisions. Each mode of operation has its advantages, but the second is especially useful for extracting ion-molecule reaction rate constants and for studying ionic equilibria. It is also useful when the gas pressure must be kept low to avoid pyrolysis or chemical attack on the hot filament.

The unique feature of icr, as compared with other widely used techniques, is its ability to determine ion-molecule reaction sequences using ion cyclotron double-resonance.[5] Even in very complex systems involving many competing reaction pathways, it is possible to sort out the various processes occurring and determine the origin of each ion appearing in the system. Much of the chemistry discussed in this thesis is very complex and would probably be uninterpretable without double-resonance techniques.

Since its origin about nine years ago, icr has been applied mostly to ion-molecule reactions of organic species, and with rather spectacular success. With the exception of the simple hydrides (NH_3, H_2O, etc.), however, relatively few inorganic molecules have been examined. About half of this thesis is concerned with the negative ion chemistry of some covalent sulfur halides, particularly SF_6. The electron attachment processes and halide ion transfer reactions which characterize these systems have important chemical implications, particularly for radiolysis experiments. Most of the remainder of the thesis describes the application of icr to the study of transition metal organometallic complexes, an important class of compounds whose ion chemistry had never been investigated. One of the prime motivations for designing and constructing a new icr spectrometer was facilitating such experiments, which had pushed previously available instrumentation past its limits. The results of these investigations are described for iron pentacarbonyl and ferrocene. The future for exciting applications of ion cyclotron resonance spectroscopy to transition metal chemistry appears exceeding bright.

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CHAPTER 2

Electron Attachment to Sulfur Hexafluoride: Formation of Stable SF_6^- at Low Pressure

Introduction

The details of electron attachment by sulfur hexafluoride have been the object of considerable attention, stimulated not only by intrinsic interest in electron attachment processes but also by the extensive use of SF_6 as an energy calibration standard for low electron energies [2-5], a detector of scattered electrons in inelastic excitation processes [5-9], an efficient electron scavenger in radiolysis experiments [10-14], and an interesting chemical reagent in halide-ion transfer reactions [8,15,16]. The reaction of SF_6 with electrons is described by the following scheme:

$$\begin{tikzcd}
SF_6 + e^-(E_{kin}) \arrow[r, shift left, "k_f"] & (SF_6^-)^* \arrow[l, shift left, "k_a"] \arrow[r, "k_d"] \arrow[d, "k_r"] \arrow[dr, "k_s{[M]}"] & SF_5^- + F \\
 & SF_6^- + h\nu & SF_6^-
\end{tikzcd}$$

The $(SF_6^-)^*$ ion, formed with rate constant k_f, contains internal excitation at least equal to the electron affinity of the molecule [17,18], and may autodetach an electron (k_a), decompose to SF_5^-(k_d), or be stabilized either by collision with a species M ($k_s[M]$), or by a radiative process (k_r). The autodetachment process in $(SF_6^-)^*$ has been especially well studied, both experimentally [19-23] and theoretically [24], and "autodetachment lifetimes" ranging between 10 μsec and 2 msec have been measured. We wish to report here an ion cyclotron resonance (icr) spectroscopy [25] investigation of electron attachment to SF_6, demonstrating a radiative mechanism which leads, at low pressure in the gas phase, to a stable SF_6^- ion. The facility for trapping ions under conditions where the time between collisions is 100 msec or more makes icr uniquely suitable for studying such processes.

Results and Discussion

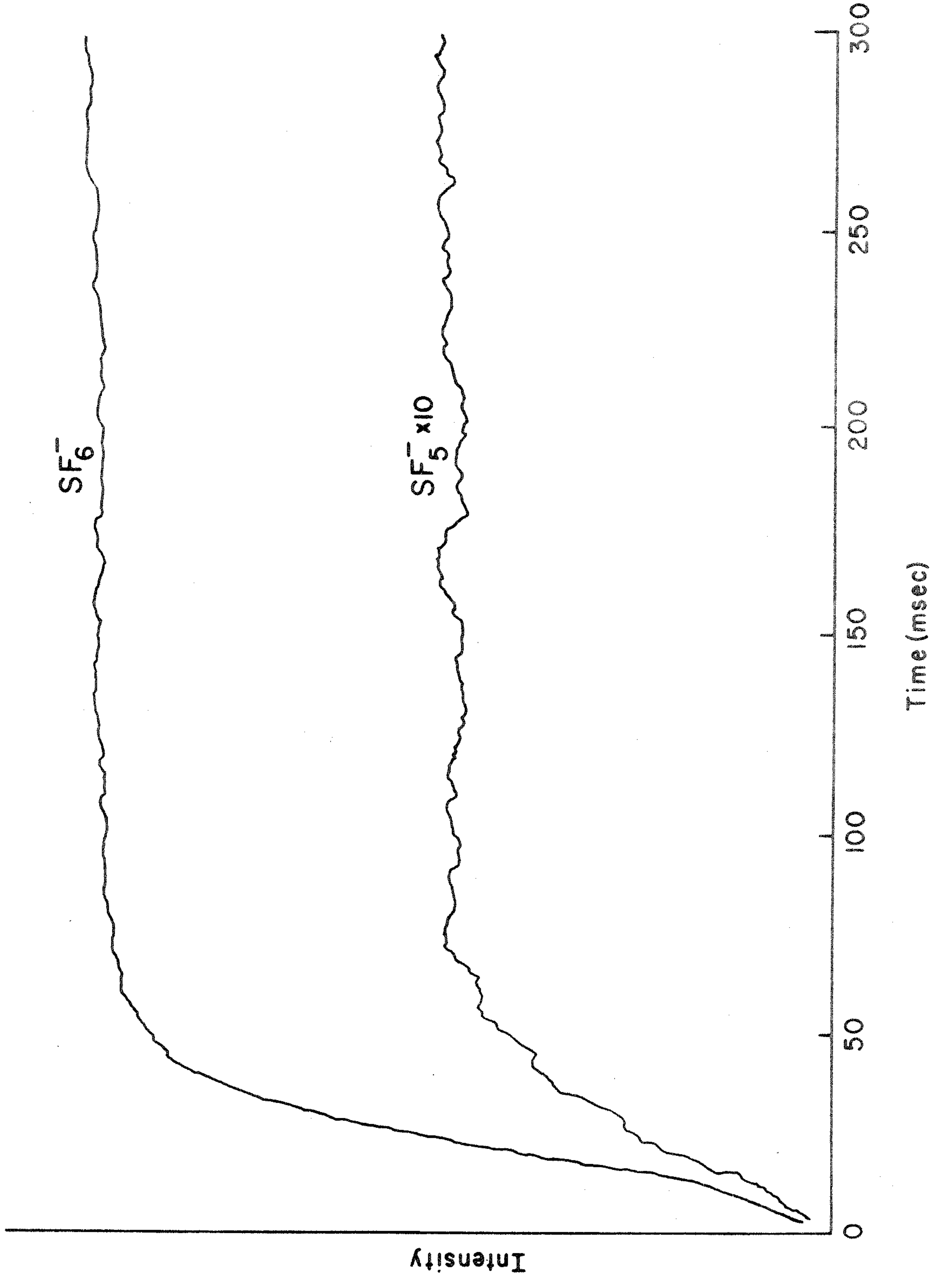
The negative-ion mass spectrum of SF_6, taken in the normal drift mode of operation at an energy of 70 eV, shows only SF_6^- and SF_5^- in appreciable abundance, in a ratio of approximately 20:1. In the icr experiment, it has been shown [22,23] that only electrons scattered from the beam and trapped in the potential well of the source region [23,26] will be attached by SF_6. Consistent with this, we find that the SF_6^- intensity increases as the nominal energy of the electron beam varies from 1 to 100 volts, higher energies resulting in more inelastically scattered electrons. All experiments described here were performed at a nominal electron beam energy of 70 volts.

Figure 1 is a trapped-ion spectrum [25] showing the intensity of SF_6^- and SF_5^- as a function of time after a 4 msec electron beam pulse at a pressure of 1.5×10^{-7} torr. After the beam pulse, the curves rise rapidly, level off at about 70 msec, and remain constant to 300 msec. As the trapping time is lengthened, ion loss begins to occur as the ions diffuse to the walls of the cell because of collisions with the background gas [27]. At this pressure and at a magnetic field of 15 kilogauss, the half life for SF_6^- ion loss is about 15 seconds.

At times longer than 20 msec, the rising SF_6^- curve in Figure 1 is accurately described by a simple exponential function, $[SF_6^-(t)] = [SF_6^-(\infty)](1 - \exp(-k_{app}[SF_6]t))$, where $[SF_6^-(\infty)]$ is the

Figure 1

Variation with time of SF_6^- and SF_5^- single resonance ion intensities following a 4 msec, 70 eV electron beam pulse in pure SF_6 at 1.5×10^{-7} torr.


Intensity
Time (msec)
0
50
100
150
200
250
300
SF_6^-
SF_5^- x10

SF_6^- ion intensity at long times, when all the electrons have been attached. The apparent bimolecular rate constant, k_{app}, for electron attachment is determined as $1.6 \pm 0.2 \times 10^{-8}$ cm^3 $molecule^{-1}$ sec^{-1}, which is independent of pressure below $\sim 5 \times 10^{-7}$ torr. Literature values for the attachment rate of thermal electrons to SF_6, determined by various methods but always in the presence of a large excess of buffer gas, are $2.4 \pm 0.6 \times 10^{-7}$ cm^3 $molecule^{-1} sec^{-1}$ [28,29]. The order-of-magnitude difference in these numbers is discussed in detail below.

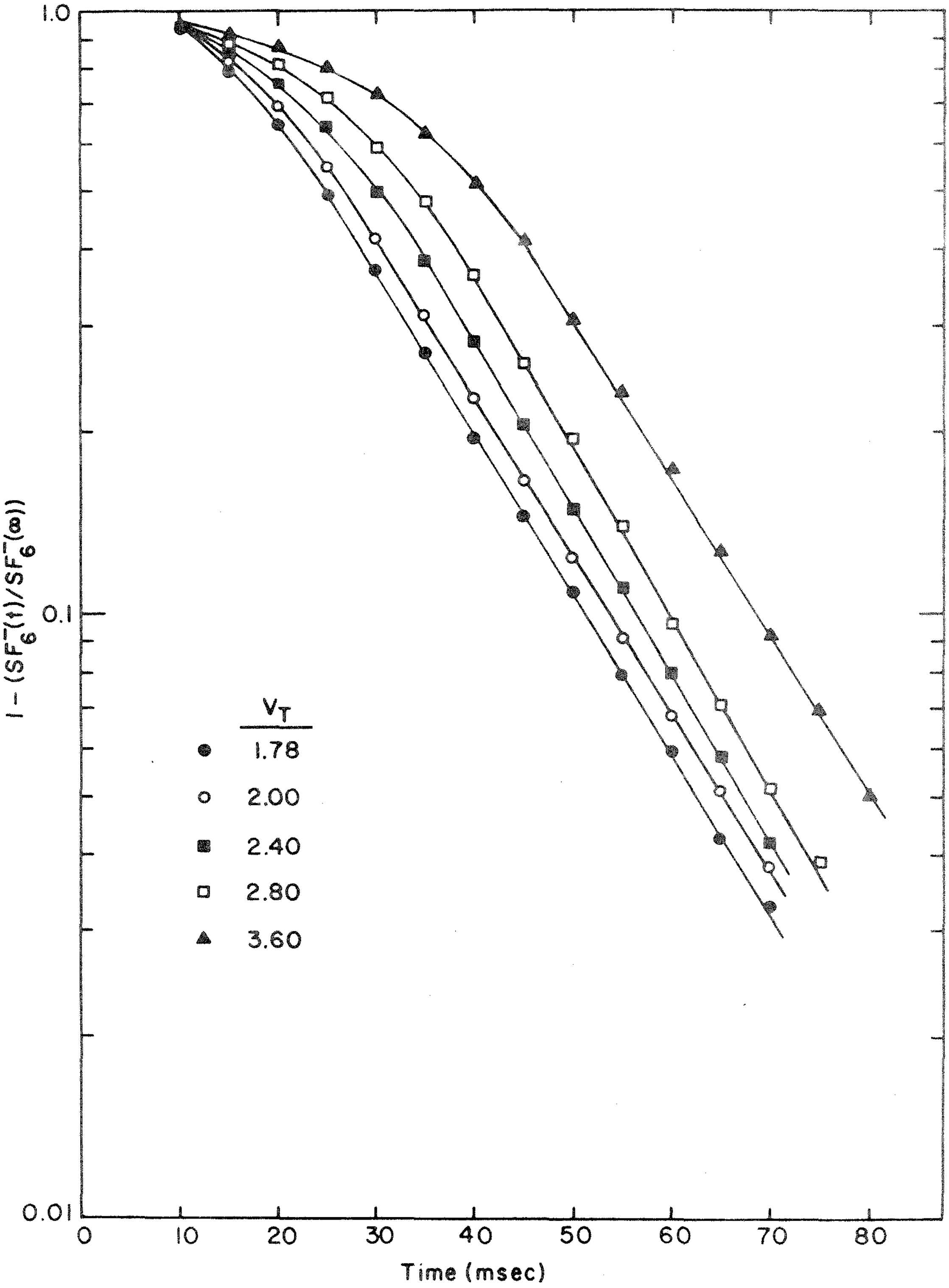
A detailed kinetic analysis of the reaction scheme above indicates that the apparent rate coefficient describing the formation of SF_6^- is a function of pressure. When the species M is not SF_6, stabilization of $(SF_6^-)^*$ by collision (rate = $k_s[M]$) will yield a larger value of k_{app} than in the absence of collisions (high pressure limit = k_f). Addition of nitrogen to the SF_6 increases k_{app} in the expected manner, up to 4.8×10^{-8} cm^3 $molecule^{-1}$ sec^{-1} at a N_2 pressure of 7.3×10^{-5} torr. In pure SF_6, however, k_{app} is predicted by the kinetic analysis to decrease with increasing SF_6 pressure, to a limiting value of k_s. In agreement with this, k_{app} decreases monotonically with added SF_6 to 2.5×10^{-9} cm^3 $molecule^{-1}$ sec^{-1} at a pressure of 1.5×10^{-5} torr. The SF_6 pressure could not be raised higher than this because the total rate of formation of SF_6^- became comparable to the sampling time of the experiment ($\sim$ 2 msec).

A problem with the simplified reaction scheme above is that k_f, k_a, and k_d are functions of the kinetic energy of the attached electron [4,24,30,31]. Thus, a question arises in this work with regard to the influence of the electron energy distribution on the measured rate of attachment. In the "flat" icr cell used in these experiments, the scattered electrons trapped in the source-region potential well will initially have a kinetic energy distribution ranging from ca. thermal to 0.9 V_T, where V_T is the trapping voltage [32]. Values of V_T used in this work ranged between -1.5 and -3.5 volts, and thus an appreciable fraction of the electrons will initially be epithermal. The average electron kinetic energy will rise with increasing V_T, and the rate of thermalization of the electrons could have a pronounced effect on the measured value of k_{app}.

To assess these effects, k_{app} was determined for a series of trapping voltages between -1.78 and -3.60 volts. The results are shown in Figure 2. It is seen that after a period of relatively slower SF_6^- formation, all the curves come to the same limiting slope. Since the rate constant describing the formation of SF_6^-, k_{app}, is calculated from the limiting slopes of these curves, the measured rate is independent of V_T and thus of the initial electron energy distribution. As expected, Figure 2 shows that the electron thermalization time increases as the distribution peaks at progressively higher energies (higher V_T). The reason that all the curves have the same limiting slope is that the electron relaxation process is evidently much faster than the attachment process, measured by k_{app}. Sulfur hexafluoride is probably particularly efficient at relaxing electrons via autodetachment of transient $(SF_6^-)^*$, leaving a vibrationally excited SF_6 neutral [20].

Figure 2

Variation of 1 - ($SF_6^-(t)/SF_6^-(\infty)$) with time at 1.3×10^{-7} torr and at various trapping voltages, V_T (in volts). Trapping voltages are negative for negative ions. $SF_6^-(\infty)$ is the SF_6^- ion intensity when all the electrons have been attached, and is equal to the number of free electrons produced during the beam pulse.


1.0
0.1
0.01
$1-(SF_6^-(t)/SF_6^-(\infty))$
0
10
20
30
40
50
60
70
80
Time (msec)
V_T
● 1.78
○ 2.00
■ 2.40
□ 2.80
▲ 3.60

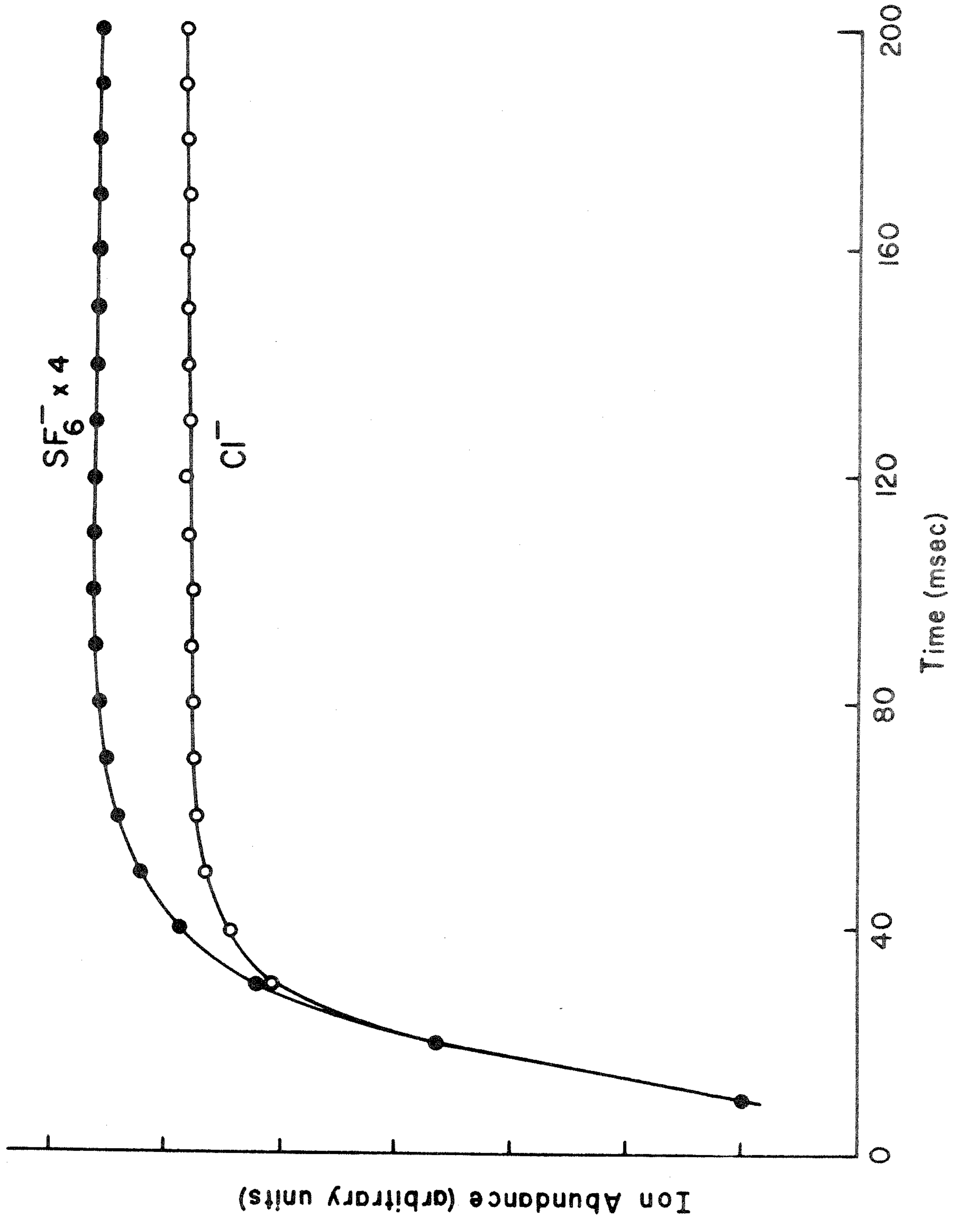
The constant SF_6^- ion intensity between 70 and 300 msec in Figure 1 suggests that one of the two stabilization mechanisms in the scheme above is operative on $(SF_6^-)^*$ in this experiment. If $(SF_6^-)^*$ were detaching an electron and being reformed continually, the gradual loss of electrons from the cell and the decomposition to SF_5^- should be manifest as a pronounced decline in SF_6^- ion intensity with time, which is not observed. The collision frequency of SF_6^- with its parent neutral can be estimated from the ion-induced dipole collision rate given by [33] $k = 2\pi\ e(\alpha/\mu)^{\frac{1}{2}} = 7.00 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}, where e = the electronic charge, α = the polarizability of $SF_6 = 6.56 \times 10^{-24}$ cm^3 [34], and μ = the reduced mass of the collision pair. At a pressure of 1.5×10^{-7} torr, the mean time between collisions is thus 200 msec. This is substantially longer than the rise time of the SF_6^- curve in Figure 1 and implies that collisional stabilization of $(SF_6^-)^*$ to SF_6^- is unimportant under these conditions. The possibility of an electron transfer reaction from $(SF_6^-)^*$ to SF_6, which might occur at a faster rate than the collision frequency, was eliminated by ejecting $^{32}SF_6^-$ from the cell and noting that no change occurred in the intensity of $^{34}SF_6^-$ as a function of trapping time. In agreement with the results of Lifshitz, et al. [18], the electron transfer reaction has a rate constant of $< 10^{-12}$ cm^3 molecule^{-1} sec^{-1}. As the only remaining possibility, a radiative process on a time scale of several milliseconds (probably involving vibrational modes) is proposed as the mechanism leading to stable SF_6^- in the low pressure trapped-ion experiment.

Unequivocal evidence for the stability of the SF_6^- ion in Figure 1 was obtained from an electron scavenging experiment in which CCl_4 was added to the SF_6. Carbon tetrachloride undergoes efficient dissociative attachment ($\sigma \cong 100$ Å^2 for thermal electrons [35]) to give Cl^- in an irreversible process. Thus, if SF_6^- autodetaches in the presence of CCl_4, a trapped-ion experiment should show a decrease in SF_6^- and an increase in Cl^- as a function of time. Figure 3 presents the data for a 3.0:1 mixture of SF_6 and CCl_4 at a total pressure of 1.8×10^{-7} torr. After about 60 msec for attachment of all the electrons, both SF_6^- and Cl^- ion intensities are constant with time. That is, the SF_6^- ion is not undergoing autodetachment. On a shorter time scale, however, Cl^- and SF_6^- are indeed coupled. Continuous ejection of SF_6^- from the cell (ejection time = 400 μsec) reduces the Cl^- intensity by 65%, i.e., under the conditions of Figure 3, at least 65% of the Cl^- ion is derived from electrons originally autodetached from (SF_6^-).

From the data of Figure 3, it is possible to calculate relative apparent rates of electron attachment by SF_6 and CCl_4. From the known ratio of neutrals (3:1) and the measured ratio of SF_6^- to Cl^- (0.28), CCl_4 is found to be 11 times more efficient in attaching electrons to give Cl^- than is SF_6 to give SF_6^- under low-pressure conditions (no collisions). Thus the rate coefficient for thermal electron attachment in CCl_4 is calculated to be $1.8 \pm 0.2 \times 10^{-7}$ cm^3 molecule^{-1} sec^{-1}. This is somewhat lower than the value of 2.8×10^{-7} cm^3 molecule^{-1} sec^{-1} reported by Christophorou and co-workers [30, 35]. Alternatively, from their determination that SF_6 and CCl_4 have the same rate of electron attachment under high-pressure conditions [30, 35], one concludes that $(SF_6^-)^*$ in the present experiment is 10 times more likely to autodetach an electron than to undergo radiative relaxation,

Figure 3

Variation with time of SF_6^- and Cl^- ion abundances following at 5 msec, 70 eV electron beam pulse in a 3.0:1 mixture of SF_6 and CCl_4 at a total pressure of 1.8×10^{-7} torr. Single resonance ion intensities have been mass corrected to give ion abundances.


$SF_6^- \times 4$
Cl^-
Ion Abundance (arbitrary units)
Time (msec)
0
40
80
120
160
200

i.e., $k_a/k_r = 10$. We have measured the rate of electron attachment in pure CCl_4 by a procedure identical to that described here for SF_6. However, CCl_4 is relatively poor at thermalizing electrons and the rate-determining step in Cl^- production is relaxation of the electron energy distribution, not the actual attachment reaction. Addition of CO_2, which is reasonably effective at thermalizing electrons, increases k_{app} (Cl^-) dramatically. At the highest CO_2 pressure employed, 3×10^{-6} torr, k_{app} had increased to 1.4×10^{-7} cm^3 molecule^{-1} sec^{-1}. The results obtained with CCl_4 are very similar to those derived by Warman and Sauer using an entirely different technique [36].

Conclusions

The distinguishing features of the present work, as opposed to previous investigations of SF_6, are (1) the experimental time scale is several orders of magnitude longer and (2) the pressure is sufficiently low that collisional processes are not significant. Formation of stable SF_6^- at low pressure is reasonably accounted for by invoking a radiative de-excitation mechanism. Such a mechanism would not be attendant to previous experiments, which involved either much shorter time scales or much higher pressures. The results indicate that caution is advisable in interpreting experiments which purport to measure autodetachment lifetimes.

The icr technique appears to be singularly well-suited for investigations of electron attachment at low pressure, in the absence of collisions, where radiative processes may be significant. Extension of the methodology described here to a variety of dissociative and non-dissociative attachment processes is in progress.

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CHAPTER 3

Chemical Consequences of Electron Scavenging by SF_6 in Radiolysis Experiments

As a result of its extremely efficient capture of thermal electrons, sulfur hexafluoride is widely used to chemically "remove" electrons from both gaseous[2-8] and liquid[9-12] radiolytic systems. In elucidating reaction mechanisms, the tacit assumption usually made is that SF_6^- is chemically inert with respect to other neutral components in the mixture. We wish to report here that, on the contrary, the SF_6^- ion is extremely reactive with a variety of acidic species which often are constituents of radiolytic systems. These results have important implications for radiolysis experiments involving use of SF_6 as an electron scavenger.

The versatile mass spectrometric technique of ion cyclotron resonance spectroscopy [13] (icr) was employed for investigating the chemical reactivity of SF_6^-. The reactant ion was formed by electron attachment to SF_6 at low pressure [14], typically 10^{-7} torr. Addition of other gases at pressures of $\sim 10^{-6}$ torr allow bimolecular encounters between SF_6^- and any desired neutral reactant, the ionic products of which can undergo further reaction on subsequent collisions. For example, in a mixture of SF_6 and HBr, reactions (1)-(6) are observed [15]. Br^- and $BrHBr^-$ are the final products in this system

$$SF_6^- + HBr \begin{cases} \xrightarrow{4\%} Br^- + HF + SF_5 & (1) \\ \xrightarrow{74\%} SF_5^- + HF + Br & (2) \\ \xrightarrow{22\%} FHBr^- + SF_5 & (3) \end{cases}$$

$$SF_5^- + HBr \begin{cases} \xrightarrow{48\%} FHBr^- + SF_4 & (4) \\ \xrightarrow{52\%} Br^- + HF + SF_4 & (5) \end{cases}$$

$$FHBr^- + HBr \longrightarrow BrHBr^- + HF \qquad (6)$$

and do not react further. A similar sequence occurs in mixtures of SF_6 and HCl, leading to $FHCl^-$ and, ultimately, to $ClHCl^-$. In this case, however, no Cl^- is produced, i.e., reactions analogous to (1) and (5) are not observed. The reaction products XHY^- are hydrogen dihalide anions, characterized by strong hydrogen bonds and concomitant high stability, and are of significant chemical interest [16, 17]. A trapped ion study [13] of the SF_6–HBr mixture, Fig. 1, shows how the various products evolve with time after a short electron beam pulse at t = 0 produces a sample of SF_6^- ions which initiate the reaction sequence according to processes (1), (2), and (3). Each reaction intermediate builds up and decays as expected from equations (1)-(6). From the slopes of the ion intensity curves, it is straightforward to extract rate constants for the various processes. Thus for reactions (1)-(6), $k_1 = 0.23$, $k_2 = 4.3$, $k_3 = 1.3$, $k_4 = 1.7$, $k_5 = 1.8$, and $k_6 = 2.4$, all in units of 10^{-10} cm^3 $molecule^{-1}$ sec^{-1} and with an estimated accuracy of 20%. Analogous rate constants in the HCl system are comparable in magnitude.

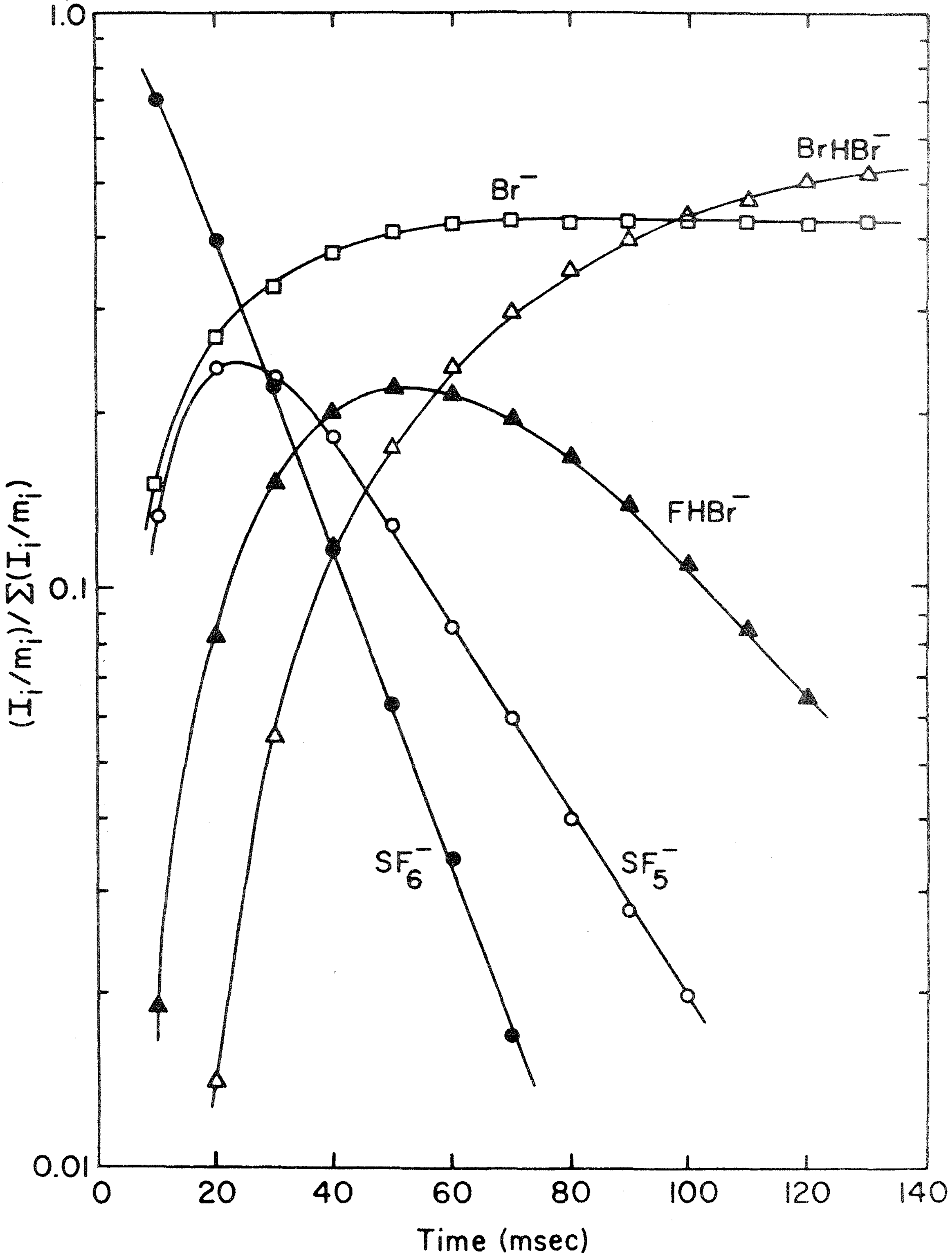
With hydrogen fluoride, SF_6^- is completely unreaction. In particular, no FHF^- is formed. This result is of kinetic origin, since fluoride ion transfer from SF_6^- to HF is definitely exothermic [18]. In the case of HI, it appears that fluoride ion transfer is followed immediately by breakup of the reaction product, since only I^- is observed [reaction (7)].

$$SF_6^- + HI \rightarrow I^- + HF + SF_5 \qquad (7)$$

This is not unexpected since F^- attachment to HX is <u>most</u> exothermic and, at the same time, dissociation of FHX^- to X^- and HF is <u>least</u>

Figure 1

Trapped-ion study of the negative ions in a 5:1 mixture of HBr and SF_6 at 1.7×10^{-6} torr. SF_6^- is formed at $t = 0$ by a 4 msec pulse of 70 volt electrons. Only Br^- originally derived from SF_5^- is included; that formed from dissociative electron attachment by HBr is excluded.


1.0
0.1
0.01
$(I_i/m_i)/\sum(I_i/m_i)$
0
20
40
60
80
100
120
140
Time (msec)
BrHBr$^-$
Br$^-$
FHBr$^-$
SF$_6^-$
SF$_5^-$

endothermic, for X = I [17].

Reactivity similar to that with HCl and HBr is observed in mixtures of SF_6 with carboxylic acids. Thus, in a mixture of SF_6 and formic acid, reactions (8)-(11) are observed. The identity of the products in reactions (9), (10), and (11) was verified by using DCO_2H

$$SF_6^- + HCO_2H \xrightarrow{25\%} SF_5^- + HF + HCO_2 \qquad (8)$$

$$SF_6^- + HCO_2H \xrightarrow{75\%} HCO_2HF^- + SF_5 \qquad (9)$$

$$SF_5^- + HCO_2H \longrightarrow HCO_2HF^- + SF_4 \qquad (10)$$

$$HCO_2HF^- + HCO_2H \longrightarrow HCO_2HO_2CH^- + HF \qquad (11)$$

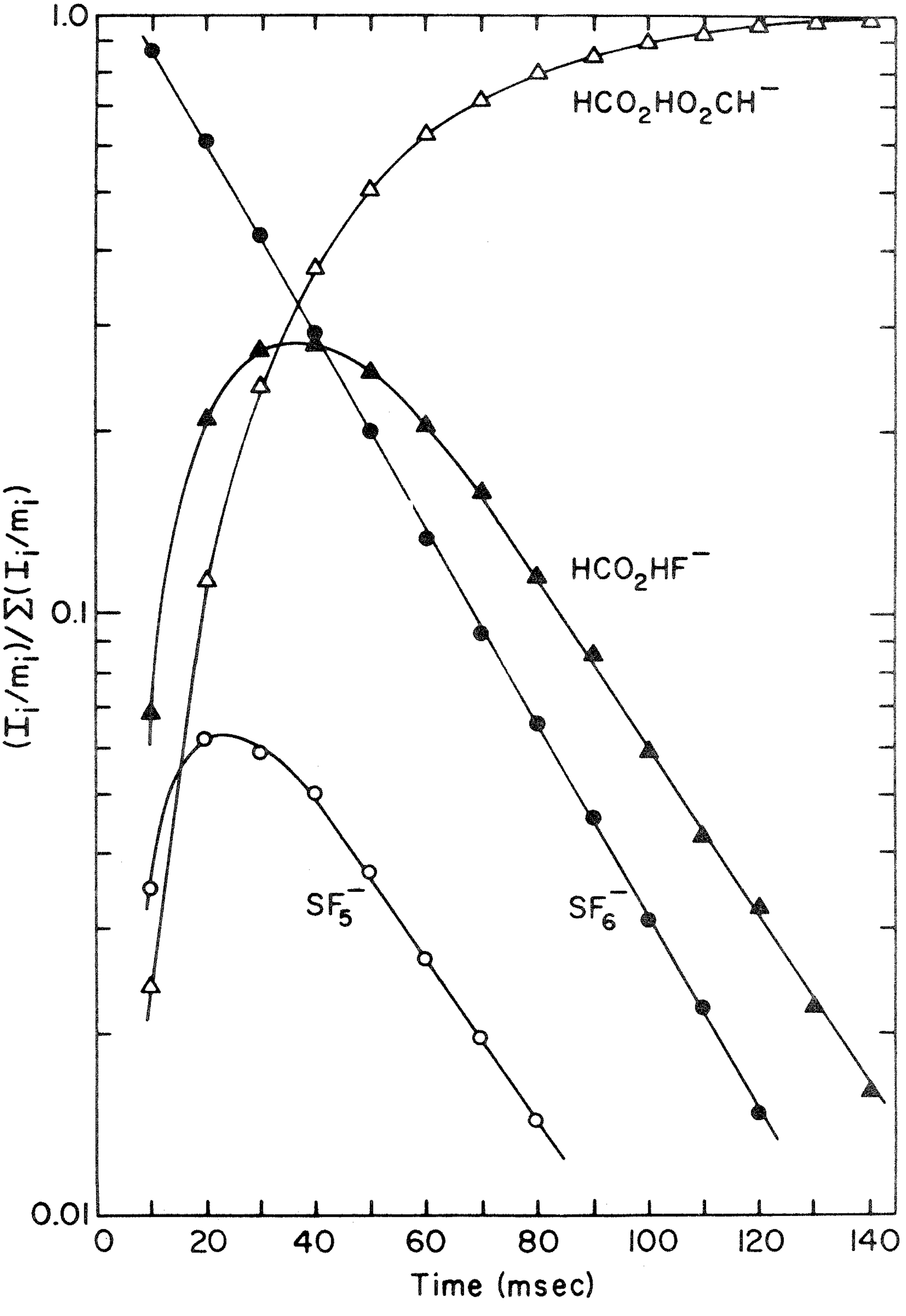
and noting that no deuterium was ever lost from any of the ionic species in equation (11). The rate constants for processes (8)-(11), determined from a trapped ion study (Fig. 2), are $k_8 = 1.1$, $k_9 = 3.2$, $k_{10} = 5.1$, and $k_{11} = 4.6$, all in units of 10^{-10} cm^3 $molecule^{-1}$ sec^{-1}. Acetic acid and SF_6 undergo an analogous sequence of reactions, resulting ultimately in the proton-bound dimer of the acetate anion, $CH_3CO_2HO_2CCH_3^-$.

Attempts to observe similar reactions in mixtures of SF_6 with H_2S, HCN, H_2O, CH_3OH, and C_2H_5OH were unsuccessful. With H_2S and HCN, only reactions (12) and (13) occur; with the others, SF_6^- appears to be unreactive.

$$SF_6 + H_2S \rightarrow SF_5^- + HF + HS \qquad (12)$$

Figure 2

Trapped-ion study of the negative ions in a 12.5:1 mixture of HCO_2H and SF_6 at 2.9×10^{-6} torr. SF_6^- is formed by a 4 msec beam pulse at t = 0.


1.0
0.1
0.01
0
20
40
60
80
100
120
140
Time (msec)
$(I_i/m_i)/\sum(I_i/m_i)$
$HCO_2HO_2CH^-$
HCO_2HF^-
SF_5^-
SF_6^-

$$SF_6 + HCN \rightarrow SF_5CN^- + HF \qquad (13)$$

The reactions noted above show that, contrary to the usual assumptions about inertness, SF_6^- can be a highly reactive ion in the presence of common acidic species, being rapidly converted to HF and XHX^- (X = Cl, Br, HCO_2, CH_3CO_2). The latter ion, formally X^- solvated by HX, has been proposed as playing a central role in the radiolysis of HCl and HBr [4-7]. Indeed, it seems probable that ions and radicals derived from SF_6 may have significant chemical effects in a variety of radiolytic systems [19]. Meaningful mechanistic inferences about radiolytic processes occurring in the presence of SF_6 should take these possible non-scavenging reactions into account.

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Reactions," J. L. Franklin, ed., Plenum Press, New York, (1972), Chapter 9. Trapped-ion techniques used in the present study are described in T. B. McMahon and J. L. Beauchamp, Rev. Sci. Instrum. 43 (1972) 509.

[14] The SF_6^- ion thus formed does not autodetach its electron, but rather is stable indefinitely. See M. S. Foster and J. L. Beauchamp, to be published.

[15] Neutral products are assumed. Only in the case of reaction (2), where the neutral product could be FHBr, is there another reasonable alternative. Similar considerations hold for the other reactions in this work.

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[17] R. Yamdagni and P. Kebarle, J. Amer. Chem. Soc. 93 (1971) 7139.

[18] M. S. Foster and J. L. Beauchamp, unpublished results. FHF^- can, however, be produced in a number of other reactions.

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CHAPTER 4

Formation and Reactions of Hydrogen Dihalide Anions in the Gas Phase

Introduction

Hydrogen dihalide anions, XHX^- and XHY^- where X and Y are halogen atoms, are distinguished by very strong hydrogen bonds and concomitant high stability.[2] As the simplest model systems for ideas about strong hydrogen bonding, these species have stimulated a substantial number of experimental[3-8] and theoretical[9-12] efforts, mostly directed at the hydrogen difluoride ion. Bond energy estimates for the symmetric XHX^- ions cover a wide range--from 12.4 kcal/mole in IHI^-[3] to 60 kcal/mole in FHF^-.[12] Almost all of the experimental data relate to spectroscopic and structural features of the ions; there are very few reports concerning their chemical behavior.

The bond energy in XHX^- can be interpreted as the strength of an acid-base complex between HX and X^-, and thus relates directly to a quantitative measurement of the Lewis acidity of HX. An obvious generalization to XHY^- follows and, indeed, to XA^-, where A is any acid. In this regard, Haartz and McDaniel have recently used relative fluoride ion affinities, measured in the gas phase, to establish an acidity order for a series of Lewis acids, mostly aprotic.[13]

The present report concerns an efficient and general method for producing XHX^- and XHY^- ions (X, Y = F, Cl, Br) at low pressure in the gas phase *via* strictly bimolecular reaction sequences. These efforts continue our investigations of the chemical consequences of strong hydrogen bonding in the gas phase,[14] utilizing the techniques of ion cyclotron resonance (icr) spectroscopy.

Experimental

The theory, techniques, and instrumentation of icr spectroscopy have been previously described in detail.[15] The instrument used in this study was built in these laboratories and incorporates a number of features making it capable of higher sensitivity and improved resolution over a wider mass range (upper limit ~ m/e 600) than previously available instrumentation.

A "flat" icr cell modified for trapped-ion studies[15] was utilized with an additional 90% open mesh grid installed between the filament and the trapping plate. The potential on this grid could be varied independently and was typically held at -6 V, while the filament bias was momentarily pulsed more negative than this to inject electrons into the cell for trapped-ion experiments. Electrons inelastically scattered from the beam are thermalized and attached as they oscillate in the potential well of the source region.[16-18] The duration of the electron beam pulse ranged between 1 and 5 msec. The circuitry necessary for performing trapped-ion experiments will be described in detail elsewhere.[19]

Trapped-ion experiments were performed in the pressure range 10^{-7} to 10^{-5} torr. To measure pressures accurately, a Schulz-Phelps type ion gauge[20] has been installed immediately adjacent to the icr cell in the magnetic field. The gauge is calibrated against an MKS Baratron Model 90H1-E capacitance manometer; a linear variation of gauge ion current with pressure is observed over two decades (10^{-5} to 10^{-3} torr). Gas mixtures were prepared directly in the instrument using independent sample inlets, with the Schulz-Phelps gauge calibrated separately for each component. The estimated uncertainty in the absolute pressure of any component (and hence in all rate constants measured) is ± 20%.

All chemicals were obtained from commercial sources and used without further purification. No impurities were apparent except in the HF sample, which contained several percent H_2O. The water, which may have originated from the walls of the inlet system, did not interfere with the negative-ion reactions studied here.

Results

The general approach employed in this work involves halide ion transfer reactions from suitable source ions to HX. The best source molecules found are covalent halides of sulfur, which attach electrons to give species capable of donating halide ions to Lewis acids. Reactions (1) - (3) illustrate the behavior of sulfur hexafluoride, sulfuryl fluoride, and sulfuryl chloride under electron impact. Reaction (1), well characterized by many investigations, proceeds with a very large cross section,[21]

$$SF_6 + e^- (\sim 0 \text{ eV}) \rightarrow SF_6^- \tag{1}$$

$$SO_2F_2 + e^- (\sim 2.5 \text{ eV}) \rightarrow SO_2F^- (29\%),\ F_2^- (11\%),\ F^- (60\%) \tag{2}$$

$$SO_2Cl_2 + e^- (\sim 0 \text{ eV}) \rightarrow SO_2Cl^- (43\%),\ Cl_2^- (8\%),\ Cl^- (49\%) \tag{3}$$

by far the largest of the three, and in the trapped-ion icr experiment yields an SF_6^- ion which is stable for many seconds.[18] Reese and co-workers[22] have studied the negative ions produced from SO_2F_2. The resonance capture cross section at ~ 2.5 eV is comparatively small and while the molecule does scavenge thermal electrons, only $SO_2F_2^-$ is formed. The relatively high pressures required to produce sufficient amounts of SO_2F^- and F_2^- precluded trapped-ion experiments with this molecule. The negative ion mass spectrum of SO_2Cl_2 does not appear to have been previously reported. The molecule captures ca. thermal energy electrons giving the ions noted in eq 3. The cross section is fairly fairly large and trapped-ion experiments are feasible with SO_2Cl_2.

Ionic products of processes (1) - (3) react with HX by transferring a halide ion. Reactions with each of the hydrogen halides will be considered separately.

HF. The negative ions derived from SO_2F_2 react with HF according to eqs 4 and 5, resulting in formation of the hydrogen difluoride ion, which does not react further. The only other negative-ion reaction

$$SO_2F^- + HF \rightarrow FHF^- + SO_2 \tag{4}$$

$$F_2^- + HF \rightarrow FHF^- + F\cdot \tag{5}$$

observed in this system is the formation of $SO_2F_3^-$ from F_2^-. The rate constants for reactions (4) and (5) were not measured accurately but are estimated to be ca. 10^{-10} cm^3 molecule^{-1} sec^{-1}.

The direct reaction of SF_6^- with HF was not observed (rate constant $< 10^{-12}$ cm^3 molecule^{-1} sec^{-1}). This result is evidently of kinetic origin since F^- transfer from SF_6^- to HF is exothermic (see below).

HCl. In contrast to HF, HCl reacts rapidly with SF_6^-. Figure 1 presents a trapped-ion spectrum of a mixture of SF_6 ahd HCl. Double resonance experiments verify processes (7) - (10),[23] consistent with the temporal behavior of the various ions in Figure 1. Product distributions were determined from ion ejection experiments.[15] From the limiting slopes of the ion intensity curves, rate constants can be calculated for

$$SF_6^- + HCl \xrightarrow{56\%} SF_5^- + HF + Cl \qquad (7)$$

$$SF_6^- + HCl \xrightarrow{44\%} FHCl^- + SF_5 \qquad (8)$$

$$SF_5^- + HCl \longrightarrow FHCl^- + SF_4 \qquad (9)$$

$$FHCl^- + HCl \longrightarrow ClHCl^- + HF \qquad (10)$$

reactions (7) - (10) (see Table I). No other reactions are observed in this system; in particular, Cl^- is not formed.

HBr. Halide ion transfer reactions analogous to those with HCl occur in a mixture of SF_6 and HBr, eqs 11 - 16. Br^- is also produced from both SF_6^- and SF_5^-. Figure 2 shows a trapped ion plot of the

$$SF_6^- + HBr \xrightarrow{4\%} Br^- + SF_5 + HF \qquad (11)$$

$$SF_6^- + HBr \xrightarrow{74\%} SF_5^- + HF + Br \qquad (12)$$

$$SF_6^- + HBr \xrightarrow{22\%} FHBr^- + SF_5 \qquad (13)$$

$$SF_5^- + HBr \xrightarrow{52\%} Br^- + SF_4 + HF \qquad (14)$$

$$SF_5^- + HBr \xrightarrow{48\%} FHBr^- + SF_4 \qquad (15)$$

$$FHBr^- + HBr \longrightarrow BrHBr^- + HF \qquad (16)$$

Figure 1

Variation with time of ion intensities following a 4 msec, 70 eV electron beam pulse in a 5.7:1 mixture of HCl and SF_6 at 1.4×10^{-6} torr total pressure. The initial curvature in the decay observed for SF_6^- is due to the formation of this species by electron attachment.

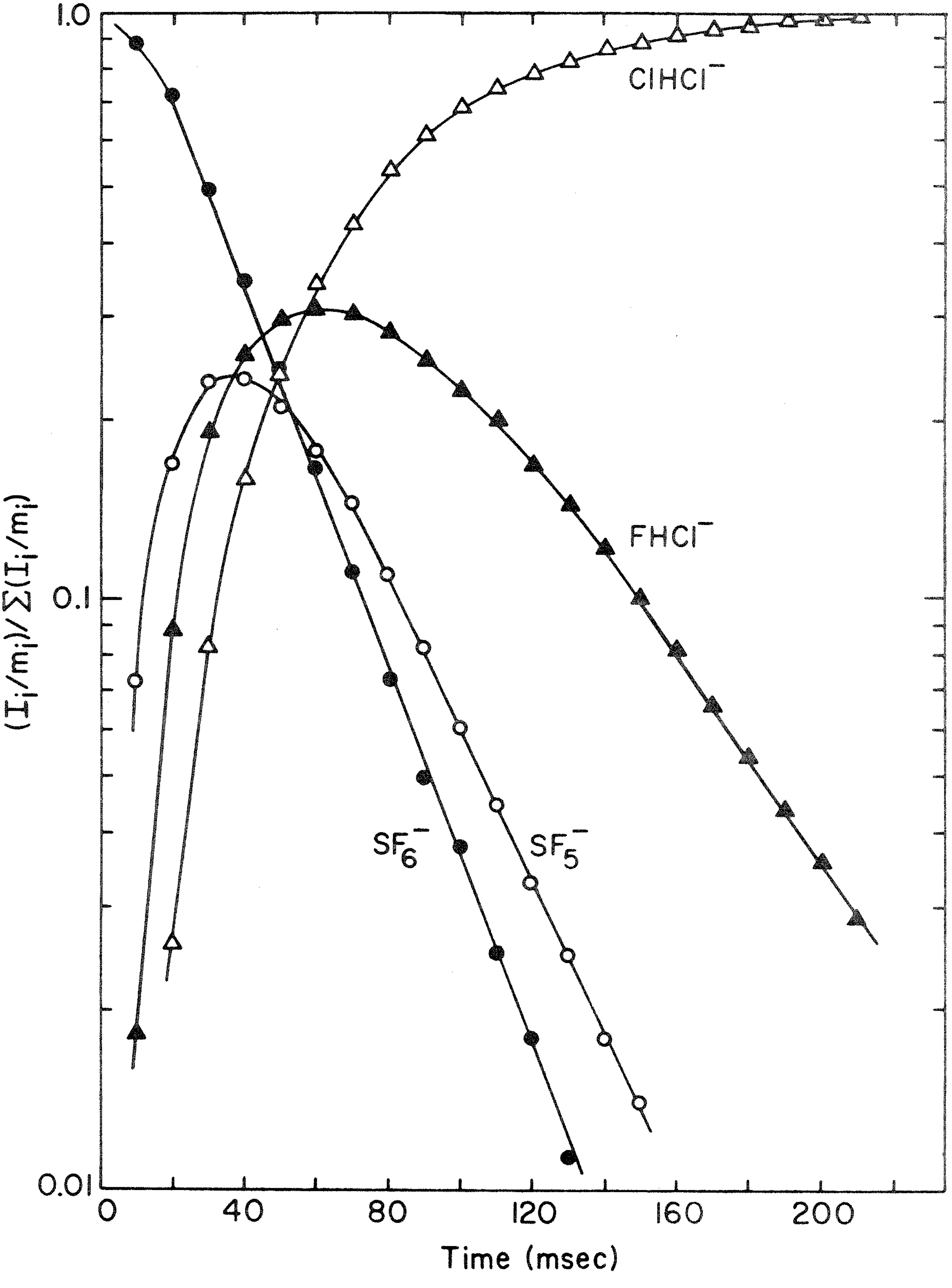

1.0
0.1
0.01
0
40
80
120
160
200
Time (msec)
$(I_i/m_i)/\sum(I_i/m_i)$
ClHCl$^-$
FHCl$^-$
SF$_6^-$
SF$_5^-$

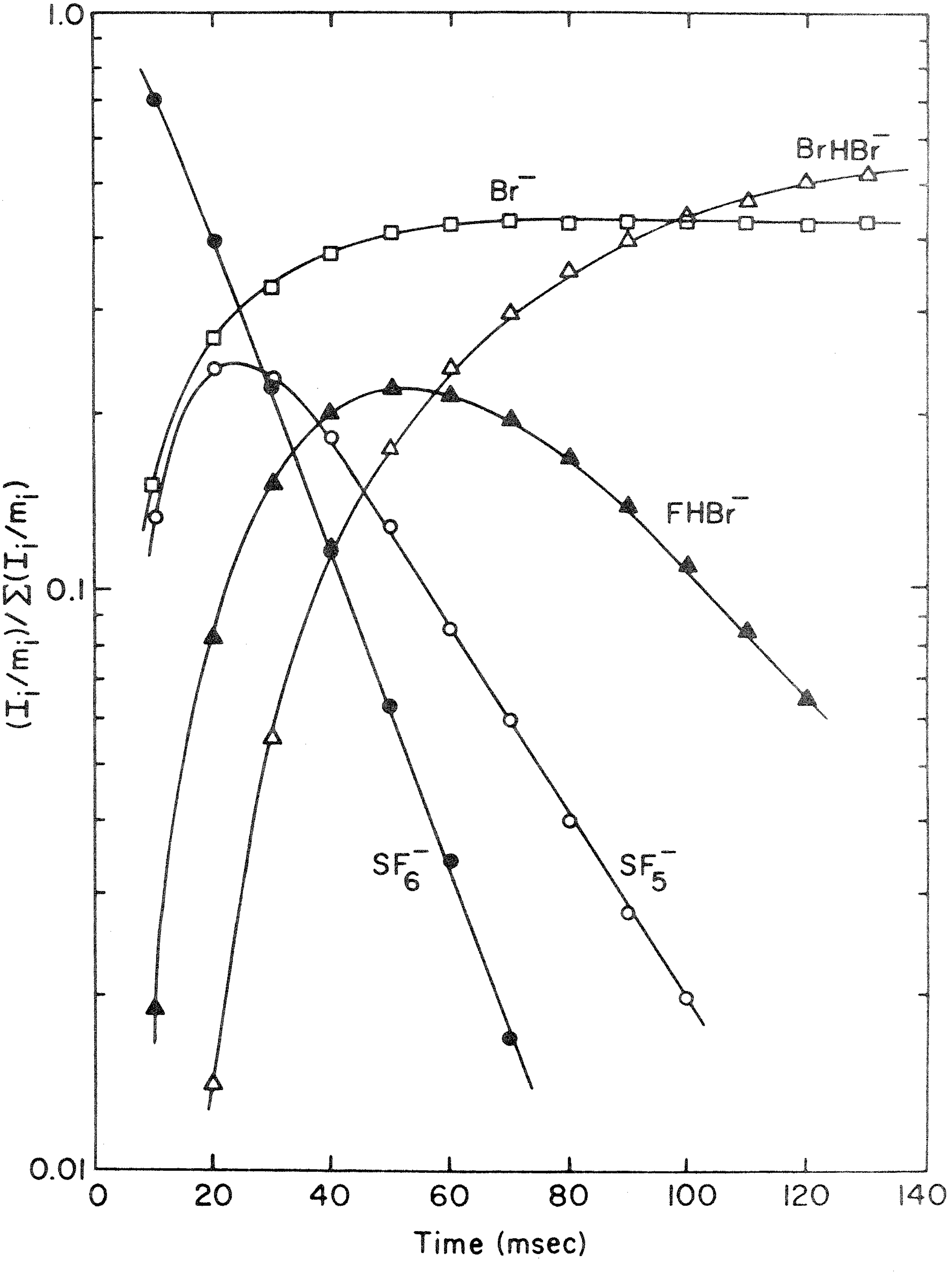
Table I. Rate Constants for Reactions Occurring in SF_6-HCl and SF_6-HBr Mixtures

Reaction	Rate Constant[a]
$SF_6^- + HCl \rightarrow SF_5^- + HF + Cl\cdot$	5.3
$SF_6^- + HCl \rightarrow FHCl^- + SF_5$	4.2
$SF_5^- + HCl \rightarrow FHCl^- + SF_4$	7.7
$FHCl^- + HCl \rightarrow ClHCl^- + HF$	5.3
$SF_6^- + HBr \rightarrow Br^- + SF_5 + HF$	0.23
$SF_6^- + HBr \rightarrow SF_5^- + HF + Br\cdot$	4.3
$SF_6^- + HBr \rightarrow FHBr^- + SF_5$	1.3
$SF_5^- + HBr \rightarrow Br^- + SF_4 + HF$	1.8
$SF_5^- + HBr \rightarrow FHBr^- + SF_4$	1.7
$FHBr^- + HBr \rightarrow BrHBr^- + HF$	2.4

[a] In units of 10^{-10} cm^3 $molecule^{-1}$ sec^{-1}. Estimated uncertainty is ± 20%.

Figure 2

Variation with time of ion intensities following a 4 msec, 70 eV electron beam pulse in a 5.1:1 mixture of HBr and SF_6 at 1.7×10^{-6} torr total pressure. Only Br^- originally derived from SF_6^- is included; that formed from dissociative electron attachment by HBr is excluded.


1.0
0.1
0.01
$(I_i/m_i)/\sum(I_i/m_i)$
0
20
40
60
80
100
120
140
Time (msec)
$BrHBr^-$
Br^-
$FHBr^-$
SF_6^-
SF_5^-

mixture. Rate constants for the halide ion transfer reactions occurring in this system are comparable in magnitude to those involving HCl (Table I).

SO_2Cl^- reacts with HBr by both halide ion transfer and halogen exchange, eqs 17 and 18. The ultimate product in this system is $BrHBr^-$; no Br^- is produced.

$$SO_2Cl^- + HBr \xrightarrow{70\%} ClHBr^- + SO_2 \qquad (17)$$

$$SO_2Cl^- + HBr \xrightarrow{30\%} SO_2Br^- + HCl \qquad (18)$$

$$ClHBr^- + HBr \longrightarrow BrHBr^- + HCl \qquad (19)$$

$$SO_2Br^- + HBr \longrightarrow BrHBr^- + SO_2 \qquad (20)$$

HI. The only reaction identified in a mixture of SF_6 and HI is (21), producing I^-. It was possible to distinguish between I^- and SF_5^- using the ^{34}S isotope. However, the signal-to-noise characteristics

$$SF_6^- + HI \longrightarrow I^- + SF_5 + HF \qquad (21)$$

were not sufficient to rule out completely reactions analogous to (12) and (14). No FHI^- or IHI^- could be detected.

Thermochemical Considerations

Heats of formation for many of the species encountered in this work are poorly known; a critical compilation of available data is presented in Table II. Using the table, several thermodynamic conclusions can be drawn from the reactions observed.

Table II. Gaseous Heats of Formation and Bond Energies at 298 °K

Species	ΔH_f^0 (kcal/mole)	Species	ΔH_f^0 (kcal/mole)
$F\cdot$	18.7 ± 0.1[a]	F^-	- 61.3 ± 0.1[f]
$Cl\cdot$	28.9[b]	Cl^-	- 55.9 ± 0.5[b]
$Br\cdot$	26.7[b]	Br^-	- 50.8[g]
$I\cdot$	25.5[b]	I^-	- 45.1[g]
HF	- 64.9 ± 0.3[a]	F_2^-	- 71.0 ± 2.3[h]
HCl	- 22.1[b]	SF_6^-	-304.4 ± 3.5[i]
HBr	- 8.7[b]	SF_5^-	-298 ± 6[j]
HI	6.3[b]		
SF_6	-291.4 ± 0.5[c]		
SF_5	-232 ± 4[d]		
SF_4	-183 ± 6[e]		

Calculated Bond Energies

Reaction	ΔH^0 (kcal/mole)
$SF_6 \rightarrow SF_5 + F\cdot$	78.1 ± 4.6
$SF_5 \rightarrow SF_4 + F\cdot$	68 ± 10
$SF_6^- \rightarrow SF_5 + F^-$	11 ± 8
$SF_6^- \rightarrow SF_5^- + F\cdot$	25 ± 10
$SF_5^- \rightarrow SF_4 + F^-$	54 ± 12

[a] Calculated from data in W. A. Chupka and J. Berkowitz, J. Chem. Phys., **54**, 5126 (1971) and J. Berkowitz, W. A. Chupka, P. M. Guyon, J. H. Holloway, and R. Spohr, J. Chem. Phys., **54**, 5165 (1971).

Table II (Continued)

[b] JANAF Thermochemical Tables, 2nd ed., Nat. Bur. Standards, NSRDS-NBS 37, 1971.

[c] Average of values given in P. A. G. O'Hare, J. L. Settle, and W. N. Hubbard, *Trans. Faraday Soc.*, **62**, 558 (1966) and V. Y. Leonidov, V. S. Pervov, O. M. Gaisinskaya, and L. I. Klyuev, *Dokl. Akad. Nauk SSSR,* **211**, 901 (1973).

[d] Based on values of D[F - SF_5] given in J. F. Bott and T. A. Jacobs, *J. Chem. Phys.*, **50**, 3850 (1969); R. K. Curran, *J. Chem. Phys.*, **34**, 1069 (1961); S. J. Riley and D. R. Herschbach, *J. Chem. Phys.*, **58**, 27 (1973).

[e] Based on J. F. Bott, *J. Chem. Phys.*, **54**, 181 (1971); D. L. Hildenbrand, *J. Phys. Chem.*, **77**, 897 (1973), ref. b.

[f] From EA(F·) = 3.400 eV, ref. a.

[g] From EA(Br·) = 3.363 eV and EA(I·) = 3.063 eV; R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, **38**, 1540 (1963).

[h] From EA(F_2) = 3.08 eV; W. A. Chupka, J. Berkowitz, and D. Gutman, *J. Chem. Phys.*, **55**, 2724 (1971).

[i] Based on EA(SF_6) = 0.57 ± 0.13 eV from C. Lifshitz, T. O. Tiernan, and B. M. Hughes, *J. Chem. Phys.*, **59**, 3182 (1973); R. N. Compton and C. D. Cooper, *J. Chem. Phys.*, **59**, 4140 (1973).

[j] Based on D[SF_5^- - F] = 1.07 ± 0.1 eV from the two references in i.

Reaction (5) sets a lower limit of 30 ± 2.5 kcal/mole on the bond energy in FHF^-. Kebarle's conclusion[8] that $D[F^- \text{-} HF] < D[F^- \text{-} HCl] =$ 50 kcal/mole establishes an upper limit and hence 30 kcal/mole < $D[F^- \text{-} HF] <$ 50 kcal/mole. Almost all other estimates[4, 5, 9-12] are higher; only the determination of 37 kcal/mole by McDaniel[5] falls in this range. With the value of Reese, et al.[22] for $\Delta H_f^0(SO_2F^-) =$ -171 kcal/mole, reaction (4) implies $D[F^- \text{-} HF] \geqslant 40$ kcal/mole. However, we do not feel Reese's number is sufficiently accurate to define a reasonable limit on the bond strength.

The bond energy $D[F^- \text{-} SF_5]$ is low and thus reactions (8) and (13) provide little information. However, $D[F^- \text{-} SF_4]$ is considerably higher, and reactions (9) and (15) imply $D[F^- \text{-} HCl]$ and $D[F^- \text{-} HBr]$ are greater than 54 ± 12 kcal/mole. Kebarle's estimate of $D[F^- \text{-} HBr] > D[F^- \text{-} HCl]$ = 50 kcal/mole is consistent with this.

Discussion

Several theoretical studies have attempted to elucidate potential surfaces for the hydrogen dihalide anions.[9-11] In the case of FHF^-, all calculations agree that for fluorine atoms separated by a distance equal to that experimentally measured, the hydrogen atom sees a single potential minimum equidistant between the fluorines. Except for one recently reported exception,[26] experimental and theoretical results have derived a linear, symmetric structure for FHF^-. In contrast, $ClHCl^-$, $BrHBr^-$, and IHI^- exhibit a shallower, double-minimum surface with a small barrier (~ 0.25 kcal/mole) between the minima.[11] In the one asymmetric ion studied, $BrHCl^-$, the surface has a single minimum, which lies closer to the chlorine atom.[11] $D[Br^- \text{-} HCl]$ is calculated to be less than $D[Br^- \text{-} HBr]$, consistent with reaction (19).

The results obtained here concerning the bond strengths in the hydrogen dihalide anions are consistent with conclusions drawn from the data of previous workers:[7, 8] the bond strength $D[X^- \text{-} HR]$ increases with increasing acidity of RH. The gas-phase acidities of HX are in the order HF < HCl < HBr and thus $D[Cl^- \text{-} HF] < D[Cl^- \text{-} HCl]$, reaction (10); $D[Br^- \text{-} HF] < D[Br^- \text{-} HBr]$, reaction (16); and $D[Br^- \text{-} HCl] < D[Br^- \text{-} HBr]$, reaction (19).

The inertness of SF_6^- toward HF is surprising in view of the data in Table II. Furthermore, we have confirmed that reaction (22) is the most prominent one observed in a mixture of SF_6 and SO_2,[25] and in conjunction with process (4) requires that direct fluoride ion transfer

$$SF_6^- + SO_2 \rightarrow SO_2F^- + SF_5 \qquad (22)$$

from SF_6^- to HF is exothermic. The slow kinetics may be related to the fact that HF is considerably less acidic in the gas phase than HCl, HBr, or HI.

The rate coefficients of the fluoride ion transfer reactions from SF_6^- to HCl and HBr are comparable to the rates observed for F^- transfer to aprotic Lewis acids such as SO_2,[22] BF_3, SiF_4, and PF_4.[27, 30] Comparison of our results with those of Dillard,[27] Haartz and McDaniel,[13] and Stockdale[30] does not show, however, any particular correlation between the rate of fluoride ion transfer and the acidity of the acceptor molecule.[13]

Reaction (23), reported by Stockdale, et al.[28] to proceed with a rate constant of 8.6×10^{-8} cm^3 molecule^{-1} sec^{-1}, was never observed in our experiments. We have no explanation for this discrepancy since their time-of-flight experiment supposedly involved thermal SF_6^- ions.

$$SF_6^- + HCl \rightarrow F_2Cl^- + (SF_4H) \tag{23}$$

However, reaction (23) is rather complex to be proceeding at roughly 100 times the Langevin collision rate for SF_6^- and HCl.

The amount of halide ion produced in the reactions of SF_6^- and SF_5^- with HX varies in the order HCl < HBr < HI. Indeed, it appears that I^- is the only product formed in the SF_6 - HI system. These results may be rationalized on the basis of the internal energy available in an excited $(FHX^-)^*$ intermediate. An extrapolation of the data of Kebarle[8] suggests that the bond strength $D[F^- \text{-} HX]$ is ~ 50, ~ 59, and ~ 67 kcal/mole for X = Cl, Br, and I, respectively. Consequently, the energy released in F^- transfer increases in going from HCl to HBr to HI. At the same time, the bond energy $D[X^- \text{-} HF]$ decreases in the same series from 14 to 13 to 12 kcal/mole. Breakup of an internally excited $(FHX^-)^*$ species thus becomes more favorable for X = I than for X = Cl. In the same vein, the lack of Br^- production in the SO_2Cl_2 - HBr system is attributable to lower $D[X^- \text{-} HBr]$ and higher $D[Br^- \text{-} HX]$ bond energies for $X^- = Cl^-$ as compared to the case $X^- = F^-$ discussed above.

The reactions discussed here offer a well-defined synthetic method for producing the symmetrical XHX^- ions (X = F, Cl, Br) as unreactive final products in the appropriate systems. The trapped-ion techniques used in forming these species are also well-suited for such spectroscopic studies of ions as photodissociation[31] and photodetachment.[32]

The facile reactions between SF_6^- and the hydrogen halides have important implications for experiments in which SF_6 is employed as an electron scavenger in the presence of acidic molecules. We have recently discussed the relevance of this work to radiolysis experiments.[29] Further investigations of the exceedingly rich ion chemistry of SF_6 are currently underway in our laboratories.

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CHAPTER 5

Ion Chemistry of Iron Pentacarbonyl

Introduction

Metal carbonyls and their derivatives occupy a prominent position in organometallic chemistry. As a result of their unusual structures and industrial catalytic importance, there has been a revival of interest in the metal carbonyls during recent years, which has stimulated the synthesis of new compounds with novel geometries and bonding schemes.[1] The present paper, however, describes the application of a modern, highly-versatile mass spectrometric method, ion cyclotron resonance spectroscopy, to one of the progenitors of carbonyl chemistry, $Fe(CO)_5$.

Ion cyclotron resonance (icr) has proven to be a powerful technique for studying the gas-phase ion-molecule reactions of many chemically interesting molecules.[2] Applied with particular success to organic species, icr is also appearing in investigations of inorganic[2a, 3] and organometallic compounds. Since our preliminary report on iron pentacarbonyl,[4] accounts by Dunbar[5] and Kevan,[6] and their co-workers, have further emphasized the utility of icr for studies of organometallics. In addition, the high pressure mass spectrometry results of Müller[7] and Schildcrout[8] suggest that further experiments in this area will prove extremely fruitful. The present paper describes in detail some ion chemistry of iron pentacarbonyl, substantially expanding the results reported previously.[4] Recently developed icr trapped-ion techniques, unavailable at the time of the earlier work, have proven extremely useful in this application. Processes described which are of particular interest include: (1) formation of polynuclear complexes containing up to four iron atoms, (2) extensive ligand substitution reactions involving both σ- and π-bonding ligands, (3) an accurate determination of the basicity of $Fe(CO)_5$, and (4) generation of unusual iron complexes in the gas phase. These experiments are performed in the absence of complicating solvation phenomena and pertain directly to the intrinsic properties and reactivity of the species considered.

Experimental

The theory and general instrumentation of icr have been described previously.[2,9] The earlier experiments[4] were performed on a modified Varian V-5900 spectrometer. The more recent work employed an instrument built in these laboratories and equipped with a 15" electromagnet capable of a maximum field of 23.4 kilogauss. Standard marginal oscillator detection[2a] was employed. The resolution deteriorates at the high masses encountered in this work (FWHM $\cong$ 3 amu at m/e 600), but it was easily capable of resolving peaks 28 mass units apart, which is all that was required above ~ m/e 200. A "flat" icr cell was used throughout.

Iron pentacarbonyl was obtained from Alfa Inorganics and used without further purification except for degassing with several freeze-pump-thaw cycles. Other chemicals were obtained from standard commercial sources and used as supplied.

The only experimental difficulty encountered was the gradual formation of a conducting path between the filament and adjacent trapping plate. This was controlled by machining a groove in the filament support block so that iron shadowed from the filament could not form a complete conducting pathway. The amount of carbon monoxide appearing in the mass spectrum was not inordinate, suggesting that sample decomposition in the inlet system was not a problem.

Results

Mass Spectrum of Iron Pentacarbonyl

The 70 eV, positive ion icr spectrum of $Fe(CO)_5$ at 5×10^{-7} torr agrees well with previous mass spectrometry results.[10] The spectrum shows approximately equal abundances of Fe^+ and $FeCO^+$, which together comprise 70% of the total metal-containing ions, and lesser amounts of $Fe(CO)_n^+$ ($n = 2 - 5$). At 20 eV, the amount of Fe^+ is greatly reduced and the $Fe(CO)_n^+$ ($n = 2 - 5$) ions increase in abundance relative to $FeCO^+$. This electron energy was employed for the investigations of ligand displacement reactions, described below.

As expected,[11] the most prominent negative ion occuring at all electron energies is $Fe(CO)_4^-$, which is accompanied by about 10% as much $Fe(CO)_3^-$. At low electron energy (~2 eV), a small amount of $Fe(CO)_2^-$ is also observed.

Ion-Molecule Reactions in Iron Pentacarbonyl

As the pressure of $Fe(CO)_5$ is raised, ion-molecule reaction products appear at m/e 224, 252, and 280. The ion at m/e 224 might reasonably be formulated as either $Fe(CO)_6^+$ or $Fe_2(CO)_4^+$; its unequivocal identification as the latter species was established from the ^{54}Fe, ^{56}Fe isotope pattern. The ions at m/e 252 and 280 are $Fe_2(CO)_5^+$ and $Fe_2(CO)_6^+$, respectively. As the $Fe(CO)_5$ pressure increases, severe pyrolysis problems become evident. The ions CO^+,

Fe^+, and $FeCO^+$ increase dramatically at higher pressures, and above about 5×10^{-5} torr completely obscure the remainder of the spectrum. Thus, the presence of reaction products above m/e 280, if any, is difficult to discern at high $Fe(CO)_5$ pressure.

To obviate this problem, recently developed icr trapped-ion techniques[9] were employed in this study. These techniques allow observation of lengthy bimolecular reaction sequences at relatively low pressure and are extremely advantageous in this application. Figure 1 presents the variation with time of the ions observed in 2×10^{-6} torr of $Fe(CO)_5$ following a 6 msec, 70 eV electron beam pulse. A host of high-mass reaction products are apparent, occuring every 28 mass units above $Fe(CO)_5^+$ to m/e 560, beyond which observations were not attempted. Double-resonance experiments at fixed trapping times (100 msec for the secondary ions and 180 msec for the tertiary and quaternary ions) establish Scheme 1

Scheme 1

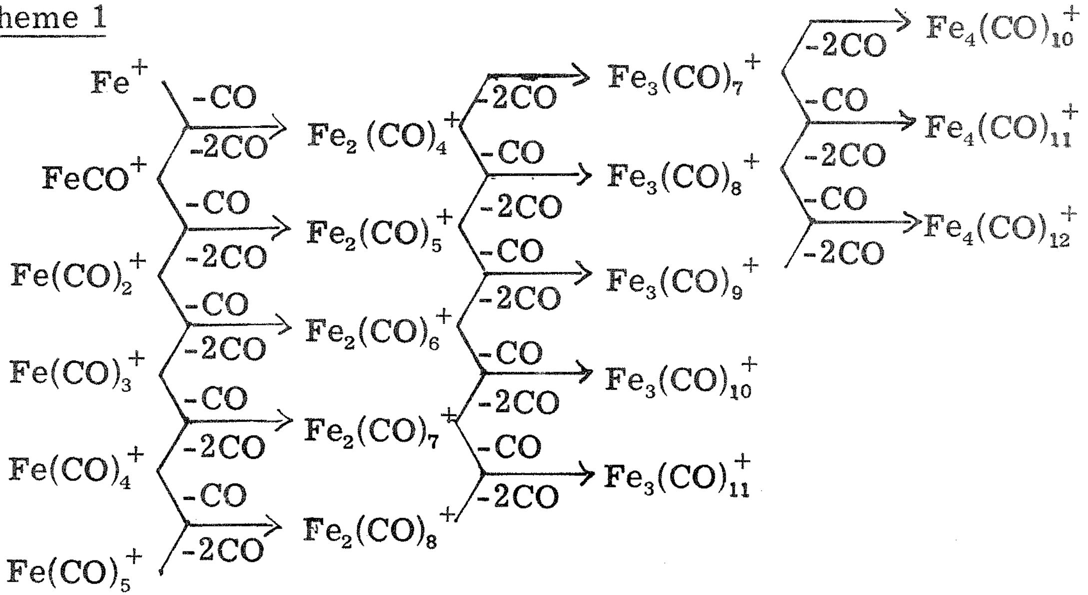
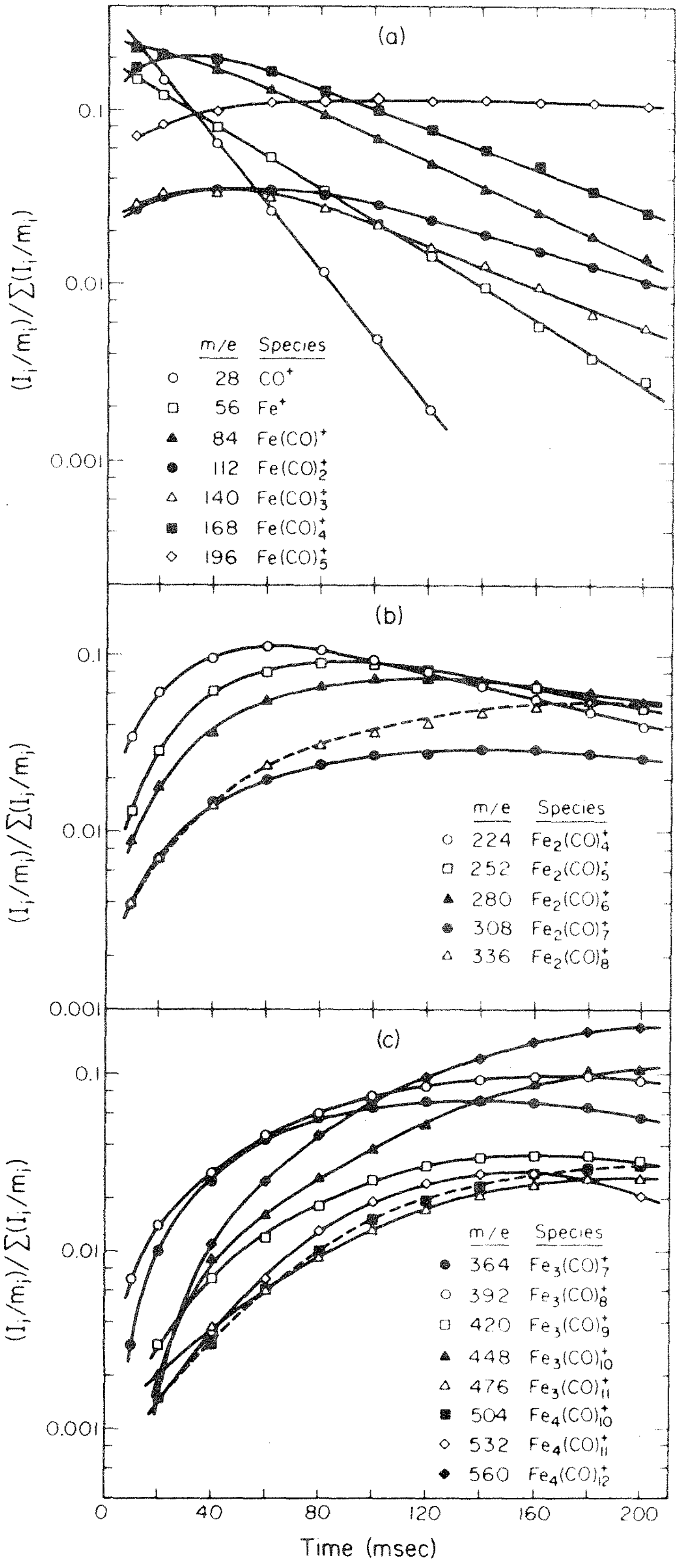


Figure 1

Variation with time of ion abundances observed in 2×10^{-6} torr of $Fe(CO)_5$ following a 6 msec, 70 eV electron beam pulse.


(a)
0.1
0.01
0.001
$(I_i/m_i)/\sum(I_i/m_i)$
m/e Species
○ 28 CO^+
□ 56 Fe^+
▲ 84 $Fe(CO)^+$
● 112 $Fe(CO)_2^+$
△ 140 $Fe(CO)_3^+$
■ 168 $Fe(CO)_4^+$
◇ 196 $Fe(CO)_5^+$
(b)
0.1
0.01
0.001
$(I_i/m_i)/\sum(I_i/m_i)$
m/e Species
○ 224 $Fe_2(CO)_4^+$
□ 252 $Fe_2(CO)_5^+$
▲ 280 $Fe_2(CO)_6^+$
● 308 $Fe_2(CO)_7^+$
△ 336 $Fe_2(CO)_8^+$
(c)
0.1
0.01
0.001
$(I_i/m_i)/\sum(I_i/m_i)$
m/e Species
● 364 $Fe_3(CO)_7^+$
○ 392 $Fe_3(CO)_8^+$
□ 420 $Fe_3(CO)_9^+$
▲ 448 $Fe_3(CO)_{10}^+$
△ 476 $Fe_3(CO)_{11}^+$
■ 504 $Fe_4(CO)_{10}^+$
◇ 532 $Fe_4(CO)_{11}^+$
◆ 560 $Fe_4(CO)_{12}^+$
0
40
80
120
160
200
Time (msec)

as the sequence of positive ion-molecule reactions in iron pentacarbonyl (the neutral reactant in each case is understood to be $Fe(CO)_5$). Either one or two CO groups are lost in each step as the various ions condense with the parent neutral. The identity of any particular product is easily determined from its precursors. For example, the ion at m/e 336 is derived exclusively from $Fe(CO)_4^+$ and $Fe(CO)_5^+$, and thus must be formulated as $Fe_2(CO)_8^+$ rather than as $Fe_3(CO)_6^+$. The product of highest mass, m/e 560, is identified as $Fe_4(CO)_{12}^+$.

Charge exchange reactions involving Fe^+ and CO^+ are observed to produce the $Fe(CO)_n^+$ (n = 1 - 5) ions, thus accounting for their initial rise in the ion intensity curves of Figure 1. Although the ionization potential of iron ($IP[Fe] = 7.90 \pm 0.01$ eV)[12] is slightly below that of iron pentacarbonyl ($IP[Fe(CO)_5] = 7.98 \pm 0.01$ eV),[10] double-resonance results indicate that $Fe(CO)_5^+$ and $Fe(CO)_4^+$ are products of a charge exchange reaction from Fe^+. This implies that some excited Fe^+ is formed by electron impact at 70 eV. The ionization potential of carbon monoxide ($IP[CO] = 14.013 \pm 0.004$ eV)[12] is much higher, and charge exchange of CO^+ with $Fe(CO)_5$ is sufficiently exothermic to rupture four of the five Fe-CO bonds in $Fe(CO)_5^+$ (see Table 1). Double-resonance results show that CO^+ reacts to produce significant amounts of $FeCO^+$ and $Fe(CO)_2^+$, smaller amounts of $Fe(CO)_3^+$ and $Fe(CO)_4^+$, and very little $Fe(CO)_5^+$. The majority of the energy released during charge exchange evidently remains in the $(Fe(CO)_5^+)^*$ species, causing successive fragmentations of this ion.

In agreement with the report of Dunbar and co-workers,[5] the only negative ion-molecule reaction observed in $Fe(CO)_5$ is process 1,

$$Fe(CO)_3^- + Fe(CO)_5 \rightarrow Fe_2(CO)_6^- + 2CO \qquad (1)$$

resulting in formation of $Fe_2(CO)_6^-$. Neither pressure variation nor trapped-ion experiments revealed any other reaction products up to m/e 420.

Ligand Displacement Reactions

Binary mixtures of $Fe(CO)_5$ with a variety of molecules were examined principally to delineate the occurrence of ligand displacement reactions. The various species considered include σ-bonding, unidentate ligands (CH_3F, CH_3Cl, H_2O, HCN, $(CH_3)_2O$, NH_3, and HCl), a σ-bonding, bidentate ligand (2,4-pentanedione), and π-bonding ligands (NO, C_2D_4, and C_6H_6). All of these experiments were performed at an electron energy of 20 volts, where each of the $Fe(CO)_n^+$ ($n = 1 - 5$) ions is reasonably abundant.

Methyl Fluoride

Mixtures of $Fe(CO)_5$ and CH_3F exhibit four prominent reaction products corresponding to the general formula $Fe(CH_3F)(CO)_{n-1}^+$ ($n = 1 - 4$). Double-resonance experiments indicate that these products are derived from the $Fe(CO)_n^+$ ions according to the generalized reaction 2,

$$Fe(CO)_n^+ + CH_3F \rightarrow Fe(CH_3F)(CO)_{n-1}^+ + CO \ (n = 1 - 4) \qquad (2)$$

which is characterized as a ligand substitution process. At the highest CH_3F pressures employed, 2×10^{-4} torr, only one CO group is replaced in any of the $Fe(CO)_n^+$ (n = 1 - 4) ions, and $Fe(CO)_5^+$ remains inert toward substitution. The products of eq. 2 condense with $Fe(CO)_5$ to give ions of the type $Fe_2(CH_3F)(CO)_x^+$. These processes, and any subsequent reactions, were not examined in detail.

Additional reaction products observed in this system are $CH_3Fe(CO)_4^+$ and $CH_3Fe(CO)_5^+$, both derived from the dimethylfluoronium ion,[13] $CH_3FCH_3^+$, in reactions 3 and 4.

$$CH_3FCH_3^+ + Fe(CO)_5 \left\{ \begin{array}{ll} \rightarrow CH_3Fe(CO)_5^+ + CH_3F & (3) \\ \rightarrow CH_3Fe(CO)_4^+ + CO + CH_3F & (4) \end{array} \right.$$

The product of eq. 3, isoelectronic with $CH_3Mn(CO)_5$, may be formulated as originating from an oxidative-addition reaction of a d^8 metal complex.[14, 15]

Methyl Chloride

In a manner analogous to that of CH_3F, methyl chloride reacts with the $Fe(CO)_n^+$ ions to give ligand displacement products according to eq. 5.

$$Fe(CO)_n^+ + CH_3Cl \rightarrow Fe(CH_3Cl)(CO)_{n-1}^+ + CO \ (n = 1 - 4) \qquad (5)$$

In this case, however, substitution does not stop after the first step, but proceeds a second time to give doubly-substituted products, process 6,

$$Fe(CH_3Cl)(CO)_{n-1}^{+} + CH_3Cl \rightarrow Fe(CH_3Cl)_2(CO)_{n-2}^{+} + CO \ (n = 3, 4) \qquad (6)$$

which do not react further. Again, $Fe(CO)_5^+$ remains inert. Substitution reactions in the binuclear and higher order complexes were not investigated for CH_3Cl or any of the other ligands discussed below.

Water

The results of adding increasing amounts of H_2O to 2×10^{-6} torr of $Fe(CO)_5$ are shown in Figure 2a-c. A large number of reaction products are observed, which correspond to sequential, multiple replacement of CO ligands by H_2O. Reactions 7-9,

$$Fe(CO)_n^+ + H_2O \rightarrow Fe(H_2O)(CO)_{n-1}^{+} + CO \ (n = 1-4) \qquad (7)$$

$$Fe(H_2O)(CO)_{n-1}^{+} + H_2O \rightarrow Fe(H_2O)_2(CO)_{n-2}^{+} + CO \ (n = 2-4) \qquad (8)$$

$$Fe(H_2O)_2(CO)_{n-2}^{+} + H_2O \rightarrow Fe(H_2O)_3(CO)_{n-3}^{+} + CO \ (n = 4) \qquad (9)$$

confirmed by double resonance, account for these products. At the highest pressure of H_2O employed, the last CO group could not be displaced from $Fe(CO)_3^+$ or $Fe(CO)_4^+$. As with CH_3F and CH_3Cl, $Fe(CO)_5^+$ remains unreactive toward ligand substitution by H_2O.

Figure 2

(a)-(c): Single resonance mass spectra at 20 eV of ions occurring in 2×10^{-6} torr of $Fe(CO)_5$ plus (a) 1×10^{-6} torr H_2O, (b) 5×10^{-6} torr H_2O, (c) 3×10^{-5} torr H_2O.

(d): Trapped-ion mass spectrum at 20 eV of a 1:2 mixture of $Fe(CO)_5$ and H_2O at 4×10^{-6} torr total pressure. Trapping time = 55 msec.

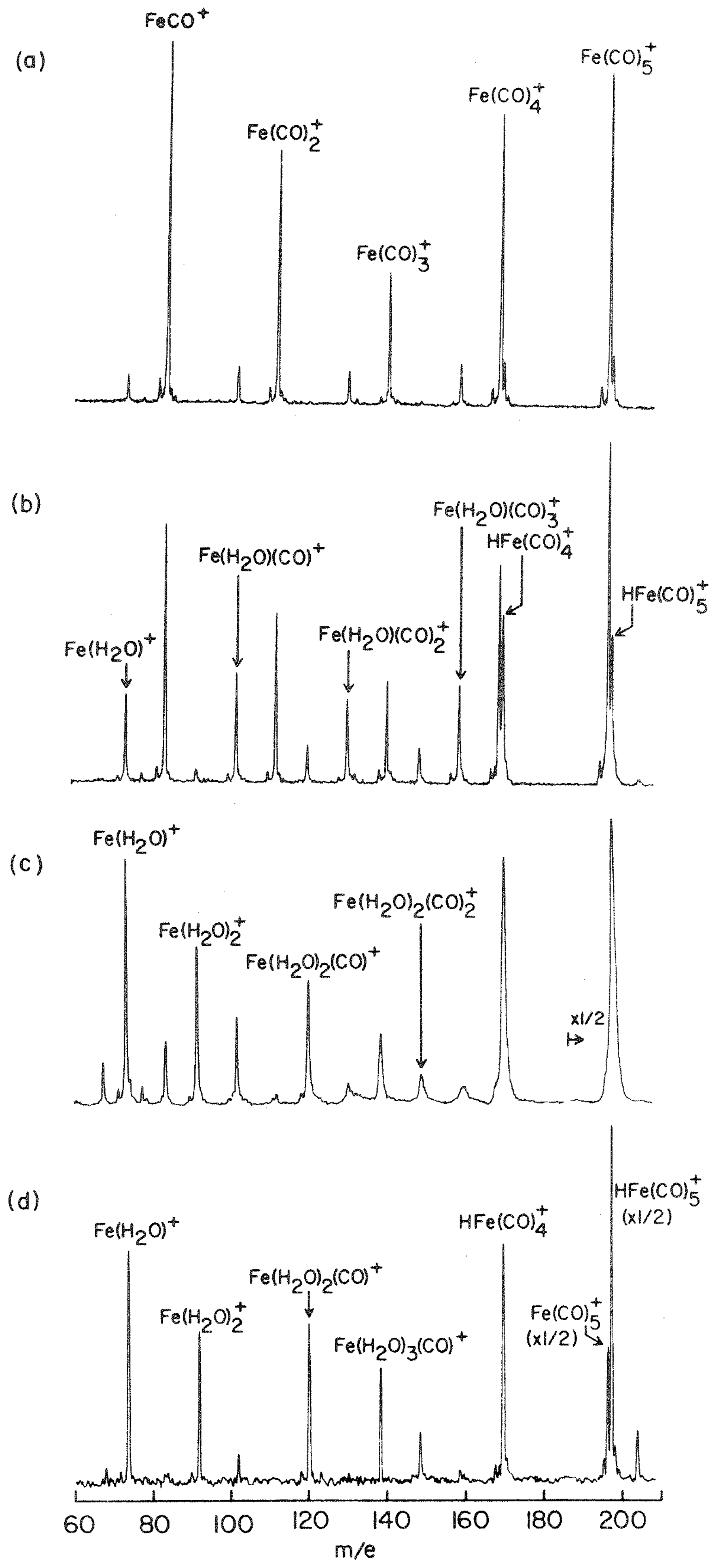

(a)
$FeCO^+$
$Fe(CO)_2^+$
$Fe(CO)_3^+$
$Fe(CO)_4^+$
$Fe(CO)_5^+$
(b)
$Fe(H_2O)^+$
$Fe(H_2O)(CO)^+$
$Fe(H_2O)(CO)_2^+$
$Fe(H_2O)(CO)_3^+$
$HFe(CO)_4^+$
$HFe(CO)_5^+$
(c)
$Fe(H_2O)^+$
$Fe(H_2O)_2^+$
$Fe(H_2O)_2(CO)^+$
$Fe(H_2O)_2(CO)_2^+$
x1/2
(d)
$Fe(H_2O)^+$
$Fe(H_2O)_2^+$
$Fe(H_2O)_2(CO)^+$
$Fe(H_2O)_3(CO)^+$
$HFe(CO)_4^+$
$HFe(CO)_5^+$
(x1/2)
$Fe(CO)_5^+$
(x1/2)
60
80
100
120
140
160
180
200
m/e

Figure 2c exhibits clearly the serious degradation of resolution (peak broadening) suffered at high pressure in the normal, drift-mode icr experiment. Trapped-ion techniques eliminate this difficulty by permitting operation at much lower pressure. Figure 2d is a mass spectrum of a 1:2 mixture of $Fe(CO)_5$ and H_2O at 4×10^{-6} torr total pressure and at a fixed ion-trapping time of 55 msec. The ions which are the final ligand substitution products in the $Fe(CO)_5$-H_2O system and which appear at high pressure in Figure 2c, are the same ones appearing in Figure 2d. However, the resolution is greatly enhanced, the spectrum is cleaner, and problems such as pyrolysis and termolecular reactions are avoided. No additional products are noted at longer trapping times.

The species $HFe(CO)_5^+$ and $HFe(CO)_4^+$, observed prominently in Figure 2, are derived by proton transfer from H_3O^+. These reactions pertain to the gas-phase basicity of iron pentacarbonyl and are discussed in detail below.

Hydrogen Cyanide

Similar, but still more extensive, ligand substitution reactions are observed in mixtures of $Fe(CO)_5$ and HCN. Processes 10-12

$$Fe(CO)_n^+ + HCN \rightarrow Fe(HCN)(CO)_{n-1}^+ + CO \ (n = 1-5) \qquad (10)$$

$$\mathrm{Fe(HCN)(CO)_{n-1}^{+} + HCN \rightarrow Fe(HCN)_2(CO)_{n-2}^{+} + CO} \quad (n = 2-4) \quad (11)$$

$$\mathrm{Fe(HCN)_2(CO)_{n-2}^{+} + HCN \rightarrow Fe(HCN)_3(CO)_{n-3}^{+} + CO} \quad (n = 3, 4) \quad (12)$$

are responsible for producing the observed products. Unlike the ligands encountered previously, HCN effects single substitution in $Fe(CO)_5^+$. Proton transfer from H_2CN^+ results in formation of $HFe(CO)_5^+$ and $HFe(CO)_4^+$.

Dimethyl Ether

Extensive ligand displacement processes also occur with CH_3OCH_3. Reactions 13-15

$$\mathrm{Fe(CO)_n^{+} + CH_3OCH_3 \rightarrow Fe(CH_3OCH_3)(CO)_{n-1}^{+} + CO} \quad (n = 1-5) \quad (13)$$

$$\mathrm{Fe(CH_3OCH_3)(CO)_{n-1}^{+} + CH_3OCH_3 \rightarrow Fe(CH_3OCH_3)_2(CO)_{n-2}^{+} + CO} \quad (n = 2-5) \quad (14)$$

$$\mathrm{Fe(CH_3OCH_3)_2(CO)_{n-2}^{+} + CH_3OCH_3 \rightarrow Fe(CH_3OCH_3)_3(CO)_{n-3}^{+} + CO} \quad (n = 4) \quad (15)$$

produce the substitution products observed. In this case, $Fe(CO)_5^+$ exchanges two of its carbonyl groups. $HFe(CO)_5^+$ is derived by proton transfer from the protonated ether, but $HFe(CO)_4^+$ is apparently not produced.

Ammonia

Addition of NH_3 to $Fe(CO)_5$ produces the same pattern of ligand substitution observed with CH_3OCH_3: The $Fe(CO)_n^+$ ($n = 2 - 5$) ions exchange twice and $Fe(CO)_4^+$ exchanges three times. Significantly, neither $HFe(CO)_5^+$ nor $HFe(CO)_4^+$ is produced in this mixture.

Hydrogen Chloride

No ligand substitution reactions were observed in a 40:1 mixture of HCl and $Fe(CO)_5$ at 10^{-4} torr. The major reaction products are $HFe(CO)_5^+$ and $HFe(CO)_4^+$, derived from H_2Cl^+ by proton transfer.

2, 4-Pentanedione

Since 2, 4-pentanedione (acetylacetone, or acac) has two n-donor sites, it might be expected to displace two CO groups upon coordinating to the metal atom in $Fe(CO)_n^+$. Indeed, this is the dominant mode of reaction observed (process 16).

$$Fe(CO)_n^+ + acac \rightarrow Fe(acac)(CO)_{n-2}^+ + 2CO \; (n = 2 - 5) \qquad (16)$$

$FeCO^+$ and $Fe(CO)_2^+$ also form complexes while losing only one CO ligand (eq. 17),

$$\mathrm{Fe(CO)}_n^+ + \mathrm{acac} \rightarrow \mathrm{Fe(acac)(CO)}_{n-1}^+ + \mathrm{CO}\ (n = 1, 2) \qquad (17)$$

but the more highly coordinated species $\mathrm{Fe(CO)}_n^+$ ($n = 3, 4, 5$) do not. The subsequent coordination of two molecules of acetylacetone proceeds in a similar manner, reaction 18.

$$\mathrm{Fe(acac)(CO)}_m^+ + \mathrm{acac} \rightarrow \mathrm{Fe(acac)}_2^+ + \mathrm{CO}, 2\mathrm{CO}\ (m = 1, 2) \qquad (18)$$

Nitric Oxide

Mixtures of $\mathrm{Fe(CO)_5}$ with the strongly π-accepting ligand NO were also examined for the occurrence of ligand substitution processes. Facile, sequential replacement of the CO groups in $\mathrm{Fe(CO)}_n^+$ was observed according to reactions 19-21.

$$\mathrm{Fe(CO)}_n^+ + \mathrm{NO} \rightarrow \mathrm{Fe(NO)(CO)}_{n-1}^+ + \mathrm{CO}\ (n = 1-5) \qquad (19)$$

$$\mathrm{Fe(NO)(CO)}_{n-1}^+ + \mathrm{NO} \rightarrow \mathrm{Fe(NO)_2(CO)}_{n-2}^+ + \mathrm{CO}\ (n = 2-4) \qquad (20)$$

$$\mathrm{Fe(NO)_2(CO)}_{n-2}^+ + \mathrm{NO} \rightarrow \mathrm{Fe(NO)_3(CO)}_{n-3}^+ + \mathrm{CO}\ (n = 3, 4) \qquad (21)$$

Significantly, the species $\mathrm{Fe(NO)(CO)}_4^+$ and $\mathrm{Fe(NO)_3(CO)}^+$ were not observed to exchange further at high pressure or long trapping times, a result discussed in more detail below.

Ethylene-d_4

Ethylene functions as a unidentate ligand in many organometallic π complexes. Addition of C_2D_4 to $Fe(CO)_5$ affords the single-substitution processes of eq. 22

$$Fe(CO)_n^+ + C_2D_4 \rightarrow Fe(C_2D_4)(CO)_{n-1}^+ + CO \ (n = 1-4) \qquad (22)$$

and the double-substitution processes of eq. 23.

$$Fe(C_2D_4)(CO)_{n-1}^+ + C_2D_4 \rightarrow Fe(C_2D_4)_2(CO)_{n-2}^+ + CO \ (n = 2-4) \quad (23)$$

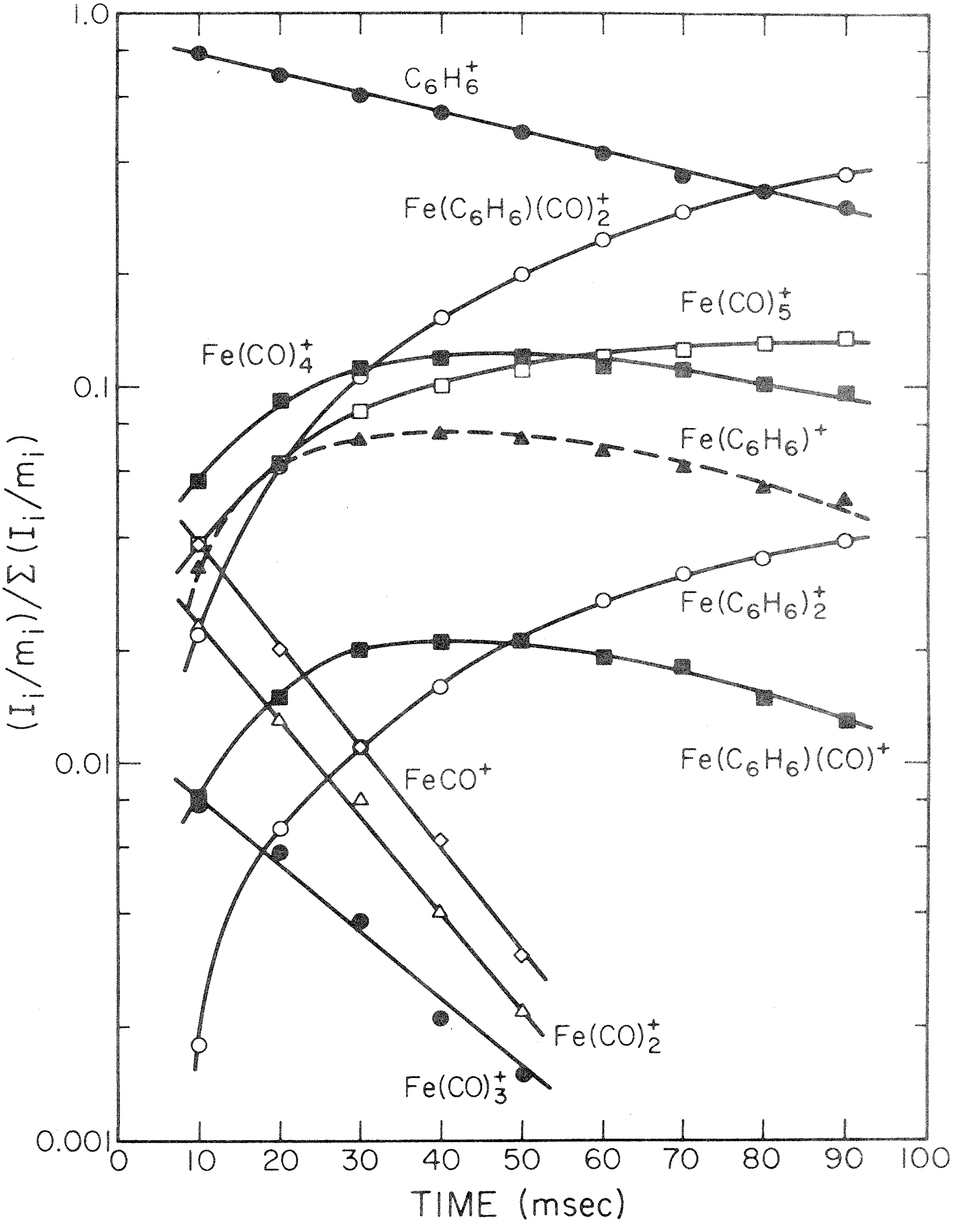
No further ligand replacement was observed, and $Fe(CO)_5^+$ remained inert towards C_2D_4.

Benzene

Mixtures of benzene with $Fe(CO)_5$ exhibit a number of ion-molecule reaction products containing C_6H_6 bound to the iron atom. Figure 3 presents the variation with time of the ions in a 1:1 mixture of C_6H_6 and $Fe(CO)_5$ following a 6 msec, 20 eV electron beam pulse. The final products in the system are seen to be $Fe(CO)_5^+$, $Fe(C_6H_6)(CO)_2^+$, and $Fe(C_6H_6)_2^+$. Double-resonance results indicate that reactions 24-29

Figure 3

Variation with time of ion abundances in a 1:1 mixture of $Fe(CO)_5$ and C_6H_6 following a 6 msec, 20 eV electron beam pulse.


1.0
0.1
0.01
0.001
0
10
20
30
40
50
60
70
80
90
100
TIME (msec)
$(I_i/m_i)/\Sigma(I_i/m_i)$
$C_6H_6^+$
$Fe(C_6H_6)(CO)_2^+$
$Fe(CO)_5^+$
$Fe(CO)_4^+$
$Fe(C_6H_6)^+$
$Fe(C_6H_6)_2^+$
$Fe(C_6H_6)(CO)^+$
$FeCO^+$
$Fe(CO)_2^+$
$Fe(CO)_3^+$

$$C_6H_6^+ + Fe(CO)_5 \rightarrow Fe(CO)_5^+ + C_6H_6 \qquad (24)$$

$$C_6H_6^+ + Fe(CO)_5 \rightarrow Fe(CO)_4^+ + CO + C_6H_6 \qquad (25)$$

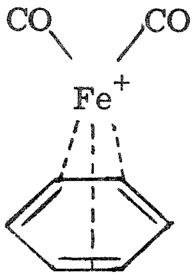
$$Fe(CO)_n^+ + C_6H_6 \rightarrow Fe(C_6H_6)(CO)_{n-1}^+ + CO \quad (n = 1, 2) \qquad (26)$$

$$Fe(CO)_n^+ + C_6H_6 \rightarrow Fe(C_6H_6)(CO)_{n-2}^+ + 2CO \quad (n = 2 - 4) \qquad (27)$$

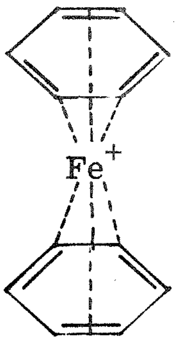
$$Fe(C_6H_6)^+ + C_6H_6 \rightarrow Fe(C_6H_6)_2^+ \qquad (28)$$

$$Fe(C_6H_6)(CO)^+ + C_6H_6 \rightarrow Fe(C_6H_6)_2^+ + CO \qquad (29)$$

are responsible for the various product ions. The charge-exchange reactions, eqs. 24 and 25, produce large quantities of $Fe(CO)_5^+$ and $Fe(CO)_4^+$ and account for the initial upward curvature of the intensity curves for these ions in Figure 3. The former species is unreactive, but $Fe(CO)_4^+$ reacts according to eq. 27 to produce $Fe(C_6H_6)(CO)_2^+$, which is the dominant ion at long times. The remaining ions all end up as $Fe(C_6H_6)_2^+$. The species $Fe(C_6H_6)(CO)_2^+$ and $Fe(C_6H_6)_2^+$ are evidently quite stable in this system and are formulated as having structures I and II, respectively.



(I)



(II)

Reactions of Anions

A number of anionic species were generated in the presence of $Fe(CO)_5$ to investigate the occurrence of nucleophilic attack on the metal complex. These included F^-, $C_2H_5O^-$, Cl^-, and CN^-, which are produced by dissociative electron capture in NF_3, C_2H_5ONO, CCl_4, and HCN, respectively. Reactions 30 and 31

$$F^- + Fe(CO)_5 \rightarrow Fe(F)(CO)_3^- + 2CO \tag{30}$$

$$C_2H_5O^- + Fe(CO)_5 \rightarrow Fe(C_2H_5O)(CO)_3^- + 2CO \tag{31}$$

were observed to result in the formation of four-coordinate, 16-electron products. Neither Cl^- nor CN^- were observed to react with $Fe(CO)_5$. This unexpected result may reflect the fact that Cl^- and CN^- are much weaker bases in the gas phase than F^- and $C_2H_5O^-$.

Basicity of Iron Pentacarbonyl

Many of the mixtures investigated for ligand substitution processes also demonstrated the formation of large amounts of protonated iron pentacarbonyl (see Figure 2, for example). Proton transfer reactions from H_2Cl^+, H_3O^+, H_2CN^+, $(CH_3)_2OH^+$, and protonated dimethyl carbonate were confirmed by double-resonance to produce $HFe(CO)_5^+$. The rates of these reactions are fast. On the other hand, addition of $Fe(CO)_5$ to NH_3 and CH_3NH_2 showed no evidence for formation of $HFe(CO)_5^+$ from NH_4^+ or $CH_3NH_3^+$, both of which were present in great abundance in their respective mixtures. In view of the fast rate of proton transfer observed in the other systems, this result is taken to indicate that proton transfer from NH_4^+ and $CH_3NH_3^+$ to $Fe(CO)_5$ is endothermic.

Discussion

Reactions in Iron Pentacarbonyl

The extensive condensation reactions which characterize the positive ion-molecule chemistry of iron pentacarbonyl are an intriguing result. The facile formation of the various polynuclear complexes in Scheme 1 must be rationalized on the basis of a strong proclivity by iron to form bonds with one or more additional iron atoms. While metal-metal bonds in carbonyl systems are rather common, the relatively non-selective nature of the reactions observed here remains surprising. That is, within the mass range studied, all of the ions condense with $Fe(CO)_5$, regardless of the number of iron atoms or CO groups already present. There seems to be no reason, in fact, to doubt that even higher order polynuclear clusters are formed.

Mass spectral investigations of polynuclear metal carbonyls generally show that the more metal atoms a fragment ion contains, the higher is its mass spectral abundance.[16] This result is interpreted as evidence for the highly favorable nature of metal-metal bonds in these species and is consistent with the icr results obtained here. The only exception to this generalization, interestingly enough, is that the mass spectra of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ show a high abundance of fragment ions containing a single iron atom and a very low abundance for those containing two iron atoms,[16] which is suggested as implying a low stability for the Fe-Fe nucleus.[17] In view of the rapid formation of $Fe_2(CO)_n^+$ (n = 4 - 8) by ion-molecule reactions, however, such a conclusion does not appear justified.

A simple MO approach to the various product ions in Scheme 1 suggests that all of them can be formulated as containing Fe-Fe multiple bonding. This is especially attractive for the symmetrical species $Fe_2(CO)_8^+$ and $Fe_4(CO)_{12}^+$, in which double-bonded iron atoms leave each metal group one electron short of the 18-electron rule.[18] The latter ion in particular is quite abundant at long times in Figure 1, suggesting that it may be significantly more stable than the other products observed. Species which would be formulated as having only

Fe-Fe single bonding, such as $Fe_2(CO)_9^+$ and $Fe_3(CO)_{12}^+$, are apparently not formed by ion-molecule reactions.

In contrast to the extensive positive ion chemistry, the negative ion chemistry of $Fe(CO)_5$ is limited to reaction 1. This is probably due at least in part to the reduced number of primary anions which can be produced in reasonable abundance from $Fe(CO)_5$ (only $Fe(CO)_3^-$ and $Fe(CO)_4^-$ in this study). Nevertheless, the non-reactivity of $Fe(CO)_4^-$ suggests a basic aversion to forming polynuclear anions in the metal carbonyls. A similar conclusion can be drawn from the work of Dunbar[5] on $Ni(CO)_4$ and $Cr(CO)_6$, which show an analogous paucity of anionic reactions.

Ligand Substitution Processes

Ligand substitution reactions in the metal carbonyls and their derivatives have been studied for many years and are probably the most thoroughly investigated aspect of their chemistry.[1, 19] Combined with various spectroscopic efforts,[19] this work has provided several general principles important to understanding the behavior of metal carbonyls:

(1) The existence of strong bonds between a metal atom and a carbonyl group hinges upon metal-CO π-bonding.[1, 19]

(2) The presence of a positive charge on a metal atom decreases metal-CO π-bonding and concomitantly increases metal-CO σ-bonding.[19, 20]

(3) Substitution of non- or poorly-π-bonding ligands into a metal carbonyl enhances π-bonding to the remaining CO groups.[1, 19]

(4) Organometallic complexes and reaction intermediates show a strong aversion to exceeding 18 valence electrons around the metal atom.[18, 19]

These four generalities are applicable to the ligand substitution reactions observed in the iron pentacarbonyl system.

In Table 1 is summarized the maximum extent of carbon monoxide replacement observed in each of the $Fe(CO)_n^+$ ions for each of the unidentate ligands considered. Also included in the table are the proton affinities (gas-phase basicities) of each of the ligands, which are defined according to eq. 32.

$$MH^+_{(g)} \rightarrow M_{(g)} + H^+_{(g)} , \quad \Delta H = PA(M) \tag{32}$$

Several observations are warranted by the data in the first eight lines of Table I (HCl through NH_3):

(1) The one molecule, HCl, which is less basic than carbon monoxide is singularly ineffective in producing any ligand substitution.

Table I. Ligand Displacement Reactions and Bond Energies in $Fe(CO)_n^+$

		Maximum number of CO groups replaced				
Ligand (L)	PA (L)[a]	$FeCO^+$	$Fe(CO)_2^+$	$Fe(CO)_3^+$	$Fe(CO)_4^+$	$Fe(CO)_5^+$
HCl	141[b]	0	0	0	0	0
CO	143[c]	--	--	--	--	--
CH_3F	151[d]	1	1	1	1	0
CH_3Cl	160[d]	1	1	2	2	0
H_2O	165[b]	1	2	2	3	0
HCN	170[b]	1	2	3	3	1
CH_3OCH_3	191[e]	1	2	2	3	2
NH_3	207[b]	1	2	2	3	2
NO	~127[c]	1	2	3	3	1
C_2D_4	160[f]	1	2	2	2	0
$D[Fe(CO)_{n-1}^+ - CO]$[g]		63	20	19	24	22

[a] Proton affinity, as defined in text, in kcal/mole at 298° K.

[b] M. A. Haney and J. L. Franklin, J. Phys. Chem., 73, 4328 (1969).

[c] A. E. Roche, M. M. Sutton, D. K. Bohme, and H. I. Schiff, J. Chem. Phys., 55, 5480 (1971).

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[e] R.H. Staley and J.L. Beauchamp, unpublished results.

[f] Ref. 2a.

[g] Bond energies in kcal/mole at 298° K from ref. 10.

(2) The higher the basicity of the ligand L, the greater the degree of substitution it can effect.

(3) While all the CO groups in $FeCO^+$ and $Fe(CO)_2^+$ are readily replaced, a maximum of three are substituted in $Fe(CO)_4^+$ and only two in $Fe(CO)_3^+$, except for the case of L = HCN.

(4) $Fe(CO)_5^+$ is much less susceptible to ligand substitution than are the other four ions.

An explanation for these observations resides in a consideration of the four general principles delineated above.

Effect of Ligand Basicity

With the possible exception of HCN (and of CO, of course) none of the ligands listed in the upper part of Table I has any recognized π-bonding ability.[21] The strength of metal-ligand bonds for such species will depend, therefore, solely on σ-bonding. On this basis the inability of HCl to displace CO is expected because of its lower basicity (poorer n-donor ability). On the other hand, each of the ligands more basic than CO is observed to displace at least one carbonyl from $Fe(CO)_n^+$ (n = 1 - 4).

That methyl fluoride can effect substitution at all suggests that the π-bonding between the iron atom and the CO groups in $Fe(CO)_n^+$

(n = 1 - 4) is minimal, which is explicable on the basis of the positive charge on the iron atom. The slightly enhanced n-donor capacity of CH_3F relative to CO (as evidenced by its greater basicity) is thus sufficient to force replacement of one CO group despite the inability of CH_3F to participate in π-bonding.

Each successive replacement of CO by a non-π-bonding ligand, however, increases the π-bonding to the remaining carbonyl groups. Thus, each step in a sequential substitution is of higher energy than the one preceding. This must be compensated for by increased σ-bonding and explains why the extent of CO substitution is directly correlated with the basicity of the entering ligand (see Table I). The enhanced π-bonding to the remaining CO group in $Fe(L)_2(CO)^+$ and $Fe(L)_3(CO)^+$ evidently makes additional substitution unfavorable. The only exception to this pattern is observed in the case of HCN, which can effect triple substitution in $Fe(CO)_3^+$. This anomaly may result from slight π-bonding ability of HCN, such as recognized for the nitriles, RCN.[21b]

The relative inertness of $Fe(CO)_5^+$ toward ligand substitution is not unexpected. The ion is coordinatively saturated, and the bimolecular substitution process would be forced to proceed through an unfavorable,[18] 6-coordinate, 19-electron intermediate. Alternatively, the carbonyl carbon atom may be susceptible to attack, but only by a sufficiently strong nucleophile (HCN, CH_3OCH_3, or NH_3). Such a situation has precedent in the substitution reactions of 6-coordinate, cationic carbonyls.[22, 23]

Π-Bonding Ligands

The π-bonding ability of nitric oxide in metal complexes is generally recognized to be even greater than that of carbon monoxide.[24] This must account for the extensive CO substitution effected by NO in $Fe(CO)_n^+$ (see Table I). All the CO groups are readily displaced in $FeCO^+$, $Fe(CO)_2^+$, and $Fe(CO)_3^+$, but only three in $Fe(CO)_4^+$ and one in $Fe(CO)_5^+$. Since NO is formally a three-electron donor,[1, 19] the products which result in the latter two cases, $Fe(NO)_3(CO)^+$ and $Fe(NO)(CO)_4^+$ are 18-electron ions, isoelectronic with $Ni(CO)_4$ and $Fe(CO)_5$. This should endow these ions with great stability against further reaction. Most of the ionic species encountered previously have had 17 or fewer electrons in the valence shell of the metal.

Ethylene also has well-recognized π-bonding ability and forms a large number of organometallic complexes (μ-complexes).[1, 19] Inspection of Table I, however, shows that C_2D_4 is not significantly more effective in producing ligand substitution than is CH_3Cl, which has the same proton affinity. Thus, the π-bonding ability of C_2D_4 does not appear to play a significant role in its CO displacement reactions.

This may result from ethylene's having only one π^* orbital available for back-bonding to the metal, whereas carbon monoxide and nitric oxide each have two.

As a ligand, benzene is usually considered to be a six-electron donor, occupying three coordination sites around a metal atom. The species $Fe(C_6H_6)(CO)_2^+$, observed prominently in Figure 3, is thus a 17-electron, 5-coordinate ion. Following this reasoning, $Fe(C_6H_6)_2^+$ is a 19-electron, 6-coordinate species, the only such ion encountered in this work. It appears as a final reaction product (Figure 3) and thus evidences greater stability than its precursors, which are 13- and 15-electron species (reactions 28 and 29). The 17-electron product, $Fe(C_6H_6)(CO)_2^+$, is evidently more stable, however, since reaction 33

$$Fe(C_6H_6)(CO)_2^+ + C_6H_6 \rightarrow Fe(C_6H_6)_2^+ + 2CO \qquad (33)$$

is not observed to occur. It is possible to avoid the 19-electron interpretation of $Fe(C_6H_6)_2^+$ by ascribing to it a structure of the type $Fe(h^6 - C_6H_6)(h^4 - C_6H_6)^+$, in which one of the benzene rings is presumably located asymmetrically with respect to the iron.

Rates of Ligand Substitution

Charge exchange reactions, such as described in detail for pure $Fe(CO)_5$ and $Fe(CO)_5$-benzene, were found to be a general feature of virtually all the systems investigated. Along with the sheer complexity of the chemistry, this makes a quantitative determination of reaction rate constants for ligand substitution difficult since the primary ions are being simultaneously formed and destroyed. Nevertheless, an inspection of the data indicates that the qualitative order of rates for single substitution is $Fe(CO)_3^+ > Fe(CO)_2^+ > FeCO^+ > Fe(CO)_4^+ > Fe(CO)_5^+$. This order appears to hold for each of the unidentate ligands in Table I (except HCl and CO). An examination of the thermochemical data in Table I reveals that there is no correlation between $[Fe(CO)_{n-1}^+ - CO]$ bond energies and rates of single substitution. Furthermore, only an ill-defined correlation exists between coordination number and rate of substitution; the more highly coordinated ions $Fe(CO)_4^+$ and $Fe(CO)_5^+$, particularly the latter, are considerably less reactive than the other three species.

Basicity of Iron Pentacarbonyl

The concept of transition metal basicity seems to be a useful one for systematizing the chemistry of many metal complexes.[25, 26] In the case of iron pentacarbonyl, the greatly enhanced lability of the CO groups in acid solution has been rationalized on the basis of participation by the protonated complex.[27] Stable $HFe(CO)_5^+$ is formed only in strong-acid solutions, indicating a low basicity, and contains a metal-proton bond.[28]

The proton transfer reactions described above serve to bracket the proton affinity of $Fe(CO)_5$, which is defined according to eq. 32, within relatively narrow limits. Proton transfer from protonated dimethyl carbonate to $Fe(CO)_5$ is readily observed, but no proton transfer is seen from NH_4^+. This is interpreted to mean that $PA[(CH_3O)_2CO] < PA[Fe(CO)_5] < PA[NH_3]$. Recent results from our laboratory indicate that $PA[(CH_3O)_2CO] = 203 \pm 2$ kcal/mole,[29] and thus $PA[Fe(CO)_5]$ is assigned as 204 ± 3 kcal/mole. Iron pentacarbonyl is thus actually quite a strong base in the gas phase. The difference the gas phase and solution behavior is attributable to the understandably poor solvation of $HFe(CO)_5^+$.

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.[30]

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CHAPTER 6

Ion-Molecule Reactions and Gas-Phase Basicity of Ferrocene

Introduction

The unusual structures and bonding of dicyclopentadienyl metal complexes (metallocenes) have stimulated many mass spectral investigation of these molecules.[1,2] Of particular interest is the recent high-pressure study of ferrocene by Schildcrout,[3] 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.[4] 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.[5] 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

The general features and operating characteristics of icr instrumentation have been previously described in detail.[6] Equipped with a "flat" cell modified for trapped-ion operation,[7] the spectrometer used in the present study was constructed at Caltech and is capable of improved resolution over a wider mass range (upper limit ~ m/e 600) than previously available instruments. The pulse circuitry which permits both trapped-ion and normal drift-mode operation will be detailed elsewhere.[8]

Ferrocene was obtained from Aldrich Chemical Company 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,[9] 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°C). 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.[10] The estimated uncertainty in absolute pressures, and thus in all rate constants reported, is ± 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.[2a, b] The ions observed and their relative abundances are: $Fe(C_5H_5)_2^+$ (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 experiments[6] unambiguously identify the charge-exchange reactions, eqs. 1 and 2, and the condensation reaction, eq. 3, as occurring in this system, the latter being responsible for the product at m/e 307, which presumably has a "triple-decker sandwich" structure.[3] The parent ion

$$Fe^+ + Fe(C_5H_5)_2 \xrightarrow{k_1} Fe(C_5H_5)_2^+ + Fe \tag{1}$$

$$FeC_5H_5^+ + Fe(C_5H_5)_2 \xrightarrow{k_2} Fe(C_5H_5)_2^+ + FeC_5H_5 \tag{2}$$

$$FeC_5H_5^+ + Fe(C_5H_5)_2 \xrightarrow{k_3} Fe_2(C_5H_5)_3^+ \tag{3}$$

appears unreactive, a conclusion verified by lowering the electron energy to 11 eV, which is below the appearance potentials of Fe^+ and $FeC_5H_5^+$,[2a] 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.[3] With no neutral product, process 3 is unusual for an ion-molecule reaction occurring at fairly low pressure, but several other examples of this behavior have been noted recently.[11, 12] No protonated ferrocene is observed in pure $Fe(C_5H_5)_2$, a result discussed further below.

Recently developed icr trapped-ion techniques[7] 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 $9.8 \pm 1.0 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1} and $7.9 \pm 0.8 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}. The former is identified with k_1 and the latter with $k_2 + k_3$. The exponential rise of $Fe_2(C_5H_5)_3^+$ (see Figure 1) provides an independent determination of k_3, which is measured as $1.2 \pm 0.1 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}. Subtracting this from the total rate for disappearance of $FeC_5H_5^+$ gives $k_2 = 6.7 \pm 0.7 \times 10^{-10}$ cm^3 molecule^{-1} 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,[3] and those predicted by the Langevin polarization theory.[13] The absolute rates determined by high pressure mass spectrometry are about three times those determined by icr, a reasonably good agreement between the two very different techniques. However, the <u>ratios</u> 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 Schildcrout[3] 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

Figure 1

Variation with time of positive ions intensities in ferrocene following a 10 msec, 70 eV electron beam pulse at a pressure of 4.3×10^{-7} torr.

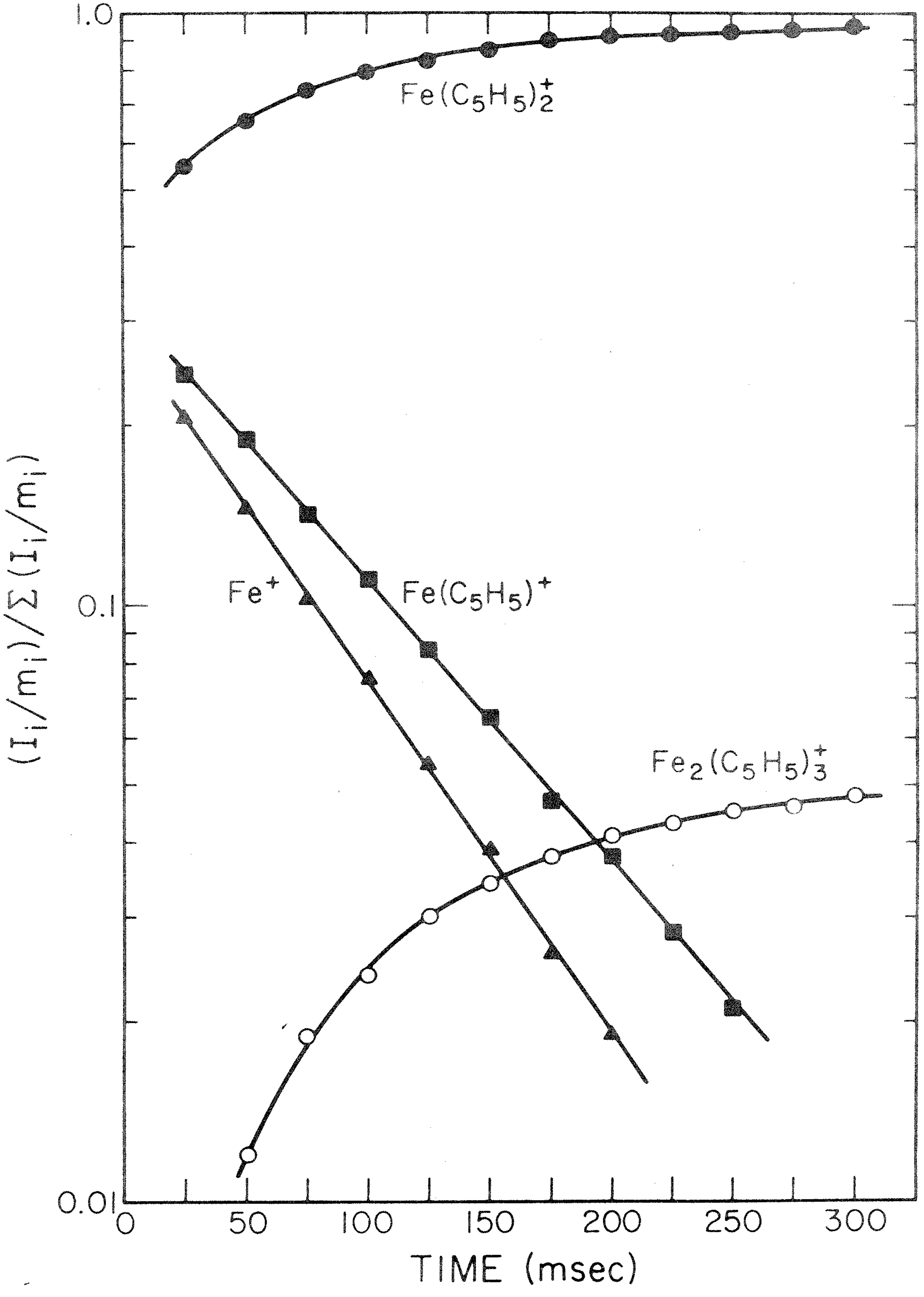
1.0
0.1
0.01
$(I_i/m_i)/\Sigma(I_i/m_i)$
$Fe(C_5H_5)_2^+$
Fe^+
$Fe(C_5H_5)^+$
$Fe_2(C_5H_5)_3^+$
0
50
100
150
200
250
300
TIME (msec)

Table I: Ion-Molecule Reactions and Rate Constants[a] in Ferrocene

Reaction	K^b	$K_s{}^c$	K/K_s	K_L^d
$Fe^+ + Fe(C_5H_5)_2 \rightarrow Fe(C_5H_5)_2^+ + Fe$	0.98 ± 0.10	2.6 ± 0.5	0.38 ± 0.11	1.55
$FeC_5H_5^+ + Fe(C_5H_5)_2 \rightarrow Fe(C_5H_5)_2^+ + FeC_5H_5$	0.67 ± 0.07	2.1 ± 0.7	0.32 ± 0.14	1.19
$FeC_5H_5^+ + Fe(C_5H_5)_2 \rightarrow Fe_2(C_5H_5)_3^+$	0.12 ± 0.01	0.34 ± 0.12	0.35 ± 0.16	

[a] All rate constants in units of 10^{-9} cm^3 $molecule^{-1}$ sec^{-1}.

[b] This work.

[c] Reference 3.

[d] Langevin polarization theory rate; see ref. 13. The molecular polarizability of ferrocene is given as 18.9×10^{-24} cm^3 in Ya. G. Dorfman, Russ. J. Phys. Chem., **37**, 1347 (1963).

uncertainty. The direct method used in the present icr experiments has proven highly accurate in previous work and is expected to yield absolute pressures to within ± 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.

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, $(i\text{-}Pr)_2O$, $CH_3N{=}NCH_3$, 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. In a mixture

$$H_3S^+ + Fe(C_5H_5)_2 \rightarrow HFe(C_5H_5)_2^+ + H_2S \qquad (4)$$

$$PH_4^+ + Fe(C_5H_5)_2 \rightarrow HFe(C_5H_5)_2^+ + PH_3 \qquad (5)$$

$$NH_4^+ + Fe(C_5H_5)_2 \rightarrow HFe(C_5H_5)_2^+ + NH_3 \qquad (6)$$

$$(i\text{-}Pr)_2OH^+ + Fe(C_5H_5)_2 \rightarrow HFe(C_5H_5)_2^+ + (i\text{-}Pr)_2O \qquad (7)$$

$$CH_3NH{=}NCH_3^+ + Fe(C_5H_5)_2 \rightarrow HFe(C_5H_5)_2^+ + CH_3N{=}NCH_3 \qquad (8)$$

of $Fe(C_5H_5)_2$ 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 $Fe(C_5H_5)_2$, CH_3NH_2, and H_2S, reaction 4 occurs readily and is followed by reaction 9 in which $HFe(C_5H_5)_2^+$ transfers a proton to CH_3NH_2. The proton affinity of a molecule M, PA(M), is defined as the

$$HFe(C_5H_5)_2^+ + CH_3NH_2 \rightarrow CH_3NH_3^+ + Fe(C_5H_5)_2 \qquad (9)$$

enthalpy change for the gas-phase reaction $MH^+ \rightarrow M + H^+$ and represents a quantitative measure of intrinsic basicity.[6,14] Thermochemical data relevant to reactions 4-9 are presented in Table II, from which the proton affinity of ferrocene is established as 212.5 ± 3.5 kcal/mole, corresponding to $\Delta H_f^0[HFe(C_5H_5)_2{}^+] = 204.8 \pm 4.8$ kcal/mole.[15]

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.[2c] 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.[16-18] Protonation only occurs in the presence of strong acids, however, suggesting a relatively low basicity for ferrocene in solution.[16,19] This has been interpreted as reflecting the rather non-specific stereochemical nature of the e_{2g} orbital.[18,19] 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.[1,5] A similar conclusion is appropriate in the case of iron pentacarbonyl, whose proton affinity has recently been measured as 204 ± 3 kcal/mole.[20] This molecule also protonates on the metal atom in solution.[21] The significantly higher basicity of $Fe(C_5H_5)_2$ relative to $Fe(CO)_5$ may reflect the fact that the metal d electrons in the carbonyl are involved in retrodative π-bonding to the CO groups and thus are not as susceptible to protonation as are

Table II: Proton Transfer Reactions Involving Ferrocene

Reaction Observed[a]	Thermochemical Inference[b]
$H_3S^+ + Fe(C_5H_5)_2 \rightarrow HFe(C_5H_5)_2^+ + H_2S$	$PA[Fe(C_5H_5)_2] \geqslant 170$[c]
$PH_4^+ + Fe(C_5H_5)_2 \rightarrow HFe(C_5H_5)_2^+ + PH_3$	$PA[Fe(C_5H_5)_2] \geqslant 188$[d]
$NH_4^+ + Fe(C_5H_5)_2 \rightarrow HFe(C_5H_5)_2^+ + NH_3$	$PA[Fe(C_5H_5)_2] \geqslant 207$[c]
$(i\text{-}Pr)_2OH^+ + Fe(C_5H_5)_2 \rightarrow HFe(C_5H_5)_2^+ + (i\text{-}Pr)_2O$	$PA[Fe(C_5H_5)_2] \geqslant 208$[e]
$CH_3NH{=}NH_3^+ + Fe(C_5H_5) \rightarrow HFe(C_5H_5)_2^+ + CH_3N{=}NCH_3$	$PA[Fe(C_5H_5)_2] \geqslant 209$[f]
$HFe(C_5H_5)_2^+ + CH_3NH_2 \rightarrow CH_3NH_3^+ + Fe(C_5H_5)_2$	$PA[Fe(C_5H_5)_2] \leqslant 216$[g]

[a] dK/dE negative in each case. Reverse reaction not observed.

[b] Values in kcal/mole. PA = proton affinity, defined in text.

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[d] Reference 11.

[e] M. Taagepera and R.W. Taft, unpublished results.

[f] M.S. Foster and J.L. Beauchamp, Int. J. Mass Spectrom. Ion Phys., in press.

[g] Reference 22.

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

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

gas-phase basicities because it is generally constant for a homologous series of molecules, leading to a linear relationship between PA(M) and IP(M).[6, 22] From the ionization potential of ferrocene (6.9 ± 0.2 eV),[2a] $D[H\text{-}Fe(C_5H_5)_2^+]$ is calculated to be 58 ± 8.5 kcal/mole. This number is extraordinarily low compared with those for other organic and inorganic molecules (which generally range between 80 and 130 kcal/mole)[6, 23] and accounts for the absence of $HFe(C_5H_5)_2^+$ in pure ferrocene. The analogous bond energy in $HFe(CO)_5^+$ is calculated to be 74.3 ± 3.2 kcal/mole, still low by comparison with other molecules but substantially higher than that in ferrocene. Not surprisingly, $Fe(CO)_5$ and $Fe(C_5H_5)_2$ can not be considered two members of a homologous series from the standpoint of $(M^+\text{-}H)$ bond energies.

It is found in all molecules studied to date that $(M^+\text{-}H)$ bond energies are greater than (M-H) bond energies in the corresponding isoelectronic neutral [e.g., $D(PH_3^+\text{-}H) > D(SiH_3\text{-}H)$].[6, 24] Such a situation may obtain for transition metal-hydrogen bonds as well: The (Mn-H) bond energy in $HMn(CO)_5$ is low, certainly less than 74 kcal/mole.[25] In view of the already weak $[H\text{-}Fe(C_5H_5)_2^+]$ bond, that in $HMn(C_5H_5)_2$ may be especially so, perhaps accounting for the fact that the latter species has never been observed while its Tc and Re analogues 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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CHAPTER 7

The Proton Affinity of Hydrogen Fluoride

Introduction

The proton affinity of a species M, defined as the enthalpy change for reaction 1, represents a quantitative measure of the intrinsic

$$MH^+_{(g)} \rightarrow M_{(g)} + H^+_{(g)}, \qquad \Delta H = PA(M) \tag{1}$$

basicity of the molecule. For two species M_1 and M_2, a knowledge of the preferred direction of the proton transfer reaction 2 establishes the

$$M_1H^+_{(g)} + M_{2(g)} \rightleftharpoons M_2H^+_{(g)} + M_{1(g)} \tag{2}$$

sign of the free energy change for the reaction, ΔG. If reaction 2 describes a system at thermal equilibrium, then the measured equilibrium constant gives ΔG according to $\Delta G = -RT \ln K$. Provided the entropic contribution $T\Delta S$ is also known, ΔH for reaction 2 is easily determined and gives directly the relative proton affinities of M_1 and M_2, i.e., $\Delta H = PA(M_1) - PA(M_2)$. An absolute measurement of either $PA(M_1)$ or $PA(M_2)$ then automatically gives the other.

The proton affinities of all the first and second row binary hydrides have been determined, with the notable exception of hydrogen fluoride. Several theoretical calculations of PA(HF) have appeared,[1, 2] but to the author's knowledge no experimental measurements of this quantity have been reported. This paper describes an ion cyclotron resonance (icr) study of proton transfer reactions occurring in mixtures of HF with several other molecules. Recently developed icr trapped-ion techniques are employed in this study and permit evaluation of a proton transfer equilibrium (eq. 2) involving H_2F^+. The basicity thus derived for hydrogen fluoride illustrates again the frequently disparate behavior of fluorine relative to the other halogens.

Experimental

The theory and instrumentation of icr spectroscopy have been previously described in detail.[3] The icr trapped-ion technique has been discussed by McMahon.[4] Basically, an electron beam is momentarily pulsed to high energy (70 eV in these experiments) to produce ions from a low pressure of sample gas (typically 10^{-6} torr). The ions are stored in the source region of the icr cell where many collisions with the background gas may result in ion-molecule reaction products. After a predetermined and variable length of time, the ions are pulsed out and mass analyzed by the normal icr procedure.[3, 4] The application of this technique to measuring equilibrium constants has been described.[5, 6]

In view of the expected propensity of hydrogen fluoride to attack the rhenium filament, HF pressures were kept less than 2×10^{-6} torr, except during pressure calibration. Even at these low pressures, HF appeared to have deleterious effects on the trapping efficiency of the "flat" icr cell used, somewhat increasing the normal rate of diffusive ion loss. Particularly adverse effects on the Schulz-Phelps ion gauge were observed during pressure calibration,[5] when the HF pressure approached 10^{-3} torr. In addition, the MKS Baratron Model 90H1-E capacitance manometer used to calibrate the ion gauge displayed greater-than-normal drift during this procedure. While the usual error in absolute pressure determination is estimated as ± 10%, in the case of HF limits of ± 50% are realistic.

Hydrogen fluoride (claimed to be anhydrous) was obtained from both Matheson Gas Products and Air Products and Chemicals. Samples were prepared and stored in stainless steel sampling cylinders, which were attached directly to the all-stainless inlet system. Low pressure icr spectra always showed the presence of water in the spectrum and H_2O^+ was frequently as much as 20% of the total ionization. Conditioning the inlet system by flowing HF through it was usually successful in reducing the H_2O^+ intensity to $<$ 5% of the total, which is approximately the amount of water present during all of the equilibrium measurements.

Results and Discussion

As expected, the only bimolecular positive ion-molecule reaction occurring in HF is process 3, the protonation reaction. A trapped-ion

$$HF^+ + HF \rightarrow H_2F^+ + F \qquad (3)$$

spectrum[4] of HF shows the expected exponential decrease in HF^+ with time and the concomitant increase in H_2F^+. The second order rate constant for reaction 3 is determined as $9.1 \pm 4.5 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1}, the 50% error estimate reflecting the uncertainty in absolute pressure. The rate coefficient calculated for eq. 3 from the Langevin induced-dipole polarization theory[7] is 1.17×10^{-9} cm^3 molecule^{-1} sec^{-1}, which is well within the estimated experimental uncertainty range. The locked-dipole approximation,[8] in which the attractive potential between

HF^+ and HF is augmented by the large dipole moment of the latter, gives a much higher rate, 6.99×10^{-9} cm^3 molecule^{-1} sec^{-1}, and does not agree with the experimental result.

Proton transfer reactions involving hydrogen fluoride were examined in binary mixtures of HF with CH_4, CO_2, and N_2. The variation of ion intensities with time following a 5 msec, 70 eV electron beam pulse in a 2:1 mixture of HF and CH_4 is shown in Figure 1. Double-resonance experiments show the expected reactions of the primary ions, eqs. 3-5.

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \tag{4}$$

$$HF^+ + CH_4 \rightarrow H_2F^+ + CH_3 \tag{5}$$

The decline with time of H_2F^+ with respect to CH_5^+ in Figure 1 suggests the occurrence of reaction 6, which was also verified by double

$$H_2F^+ + CH_4 \rightarrow CH_5^+ + HF \tag{6}$$

resonance. The reverse of process 6 could not be detected. The conclusion is that $PA(CH_4) > PA(HF)$.

Mixtures of HF with CO_2 showed an analogous sequence of reactions and the ion intensity curves resembled those of Figure 1. Proton transfer reaction 7 was observed but not its reverse, implying that

$$H_2F^+ + CO_2 \rightarrow CO_2H^+ + HF \tag{7}$$

$PA(CO_2) > PA(HF)$.

A similar experiment with nitrogen produced the results of Figure 2, which shows the variation with time of ion intensities in a 2.5:1

Figure 1

Variation with time of positive ion intensities following a 5 msec, 70 eV electron beam pulse in a 1:1 mixture of HF and CH_4 at 1×10^{-6} torr. For clarity, CH_3^+ and $C_2H_5^+$ are not shown.

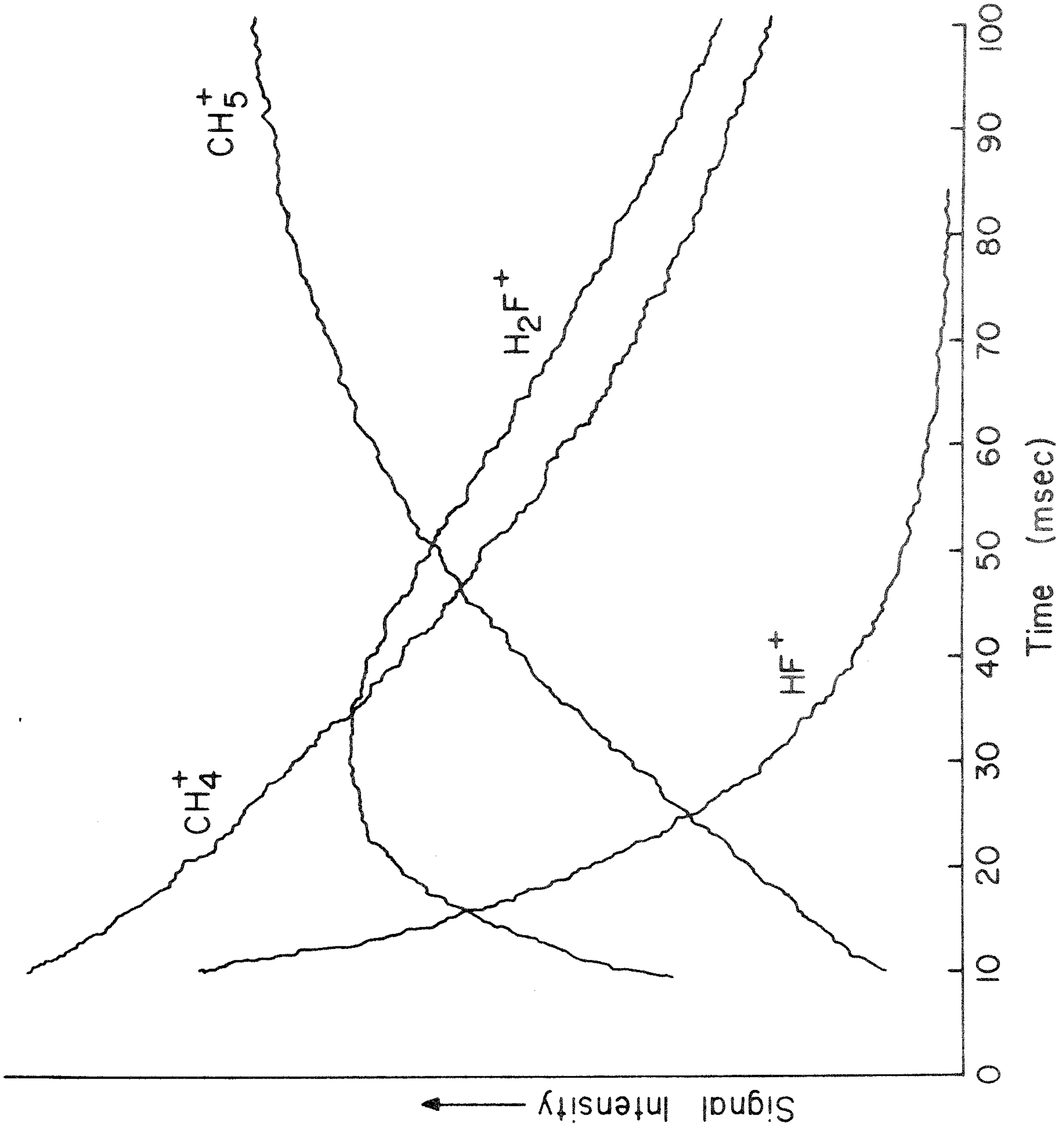
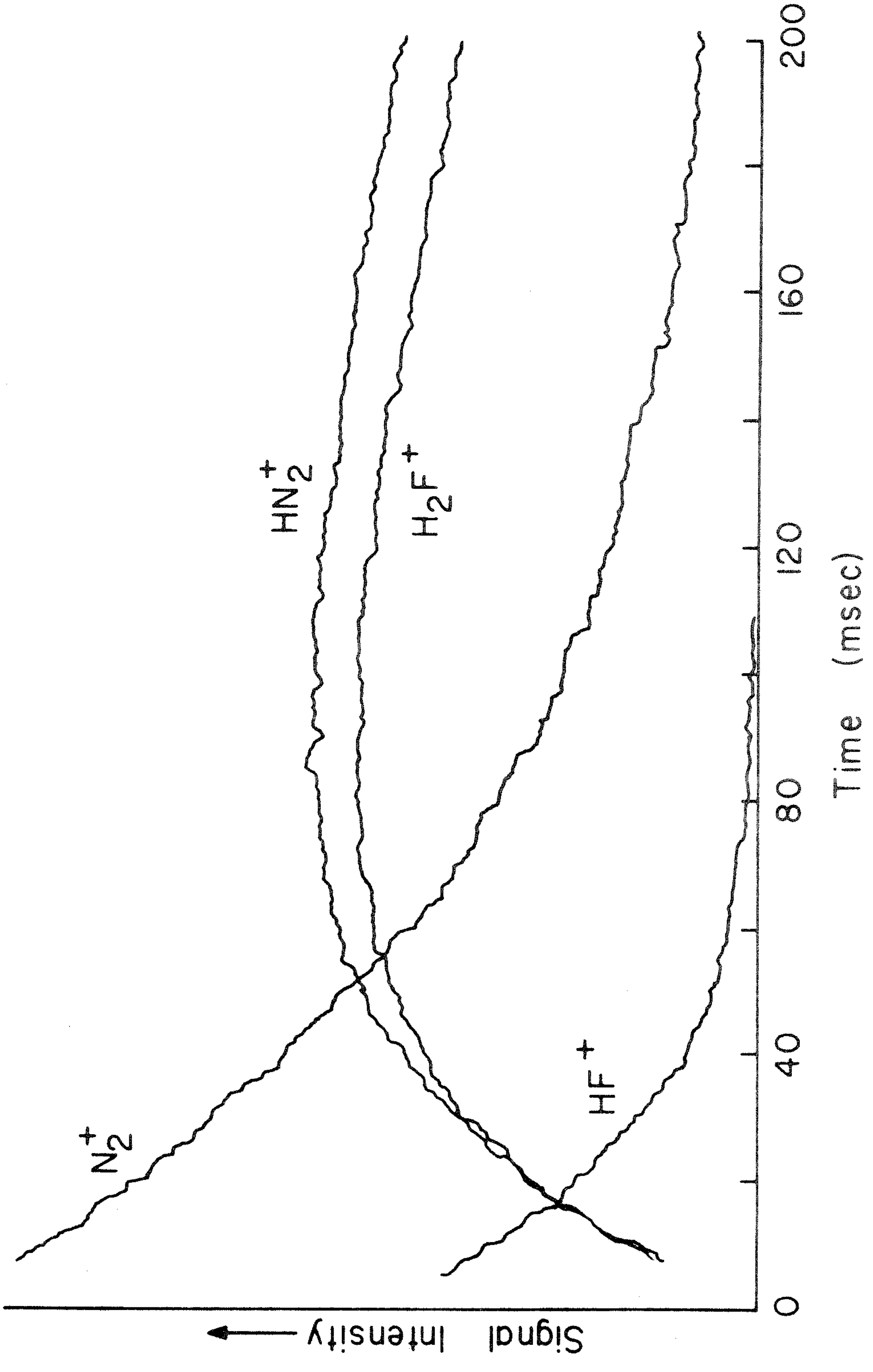

CH_4^+
CH_5^+
H_2F^+
HF^+
Signal Intensity
Time (msec)
0
10
20
30
40
50
60
70
80
90
100

Figure 2

Variation with time of positive ion intensities following a 4 msec, 70 eV electron beam pulse in a 2.5:1 mixture of HF and N_2 at 1×10^{-6} torr.


N_2^+
HF^+
HN_2^+
H_2F^+
0
40
80
120
160
200
Time (msec)
Signal Intensity

mixture of HF and N_2 at 1×10^{-6} torr. In this case, the ion intensities of H_2F^+ and HN_2^+ remain relatively constant with time out to 200 msec. Double resonance of HN_2^+ and H_2F^+ shows very strong responses in both directions (i.e., reaction 8). The gradual decrease with time of

$$H_2F^+ + N_2 \rightleftharpoons HN_2^+ + HF \qquad (8)$$

both ions reflects diffusive ion less (which is slightly faster for the lighter H_2F^+),[9] and also reaction with the H_2O impurity to form H_3O^+.

Since reaction 8 is observed to proceed in both directions, the relatively constant ratio of the HN_2^+ and H_2F^+ ion intensities in Figure 2 is interpreted as reflecting an equilibrium situation. From the known ratio of neutral pressures and the measured ratio of ion abundances (derived from Figure 2 by dividing ion intensity by ion mass), the equilibrium constant for eq. 8 is determined as 2.0 ± 1.0, corresponding to a ΔG for the reaction of -0.41 ± 0.41 kcal/mole. Over a period of 18 months, four independent measurements of the equilibrium constant gave results of 2.0 ± 1.0, 4.0 ± 2.0, 2.7 ± 1.4, and 4.5 ± 2.8. The average of these values gives $K = 3.3 \pm 1.6$ and $\Delta G = -0.81 \pm 0.40$ kcal/mole for reaction 8 as written.

The entropy contribution to reaction 8, knowledge of which is necessary to extract ΔH, can be estimated by assuming the entropies of the ionic species to be equal to those of the isoelectronic neutrals, i.e., $S(HN_2^+) = S(HCN)$ and $S(H_2F^+) = S(H_2O)$. With this assumption, $T\Delta S = -0.36$ kcal/mole for eq. 8, yielding $\Delta H = -1.07 \pm 0.40$ kcal/mole.[10] Thus, the proton affinity of nitrogen is greater than that of hydrogen fluoride by this amount.

The proton affinities of methane and carbon dioxide appear reasonably well established. PA(CH_4) is 1.5 ± 0.1 kcal/mole higher than PA(CO_2)[11] and absolute values for both are approximately 127 kcal/mole.[12, 13] Equations 6 and 7 thus provide essentially the same upper limit on the proton affinity of hydrogen fluoride: PA(HF) $<$ 127 kcal/mole.

The proton affinity of nitrogen can be estimated by several methods. Observation of ion-molecule reactions brackets PA(N_2) between 113 and 127 kcal/mole.[14] The theoretical calculation of 118 ± 3 kcal/mole by Forsen and Roos falls in this range.[15] With a flowing afterglow apparatus, Bohme and co-workers[16] have measured an equilibrium constant of $9.3 \pm 4.0 \times 10^8$ for reaction 9. This corresponds to $\Delta G = -12.2 \pm 0.3$ kcal/mole and from the entropies of H_3^+,[17] N_2,[10]

$$H_3^+ + N_2 \rightleftharpoons HN_2^+ + H_2 \qquad (9)$$

HN_2^+(= HCN),[10] and H_2,[10] $T\Delta S$ is calculated as -0.5 kcal/mole yielding $\Delta H = -12.7 \pm 0.3$ kcal/mole for reaction 9. Adopting a value of 100 ± 1 kcal/mole for PA(H_2),[17-19] the proton affinity of nitrogen is estimated by this procedure to be 112.7 ± 1.3 kcal/mole. Bohme[20] has suggested 113.6 ± 1.6 kcal/mole for PA(N_2). For the purpose of this discussion, a value of PA(N_2) = 113 ± 2 kcal/mole will be adopted, and thus PA(HF) = 112 ± 2.4 kcal/mole.

This result provides an interesting comparison with the other hydrogen halides. Table I presents available proton affinity data for HX and CH_3X molecules (X = F, [illegible] Br, I). Two relevant observations

Table I: Proton Affinities, Hydrogen Affinities, and Ionization Potentials of Hydrogen Halides and Methyl Halides[a]

X	PA(HX)	PA(CH_3X)[d]	ΔPA	IP(HX)	HA(HX^+)[g]	D(X-H)	HA(CH_3X^+)[g]
I	145[b]	170	25	240[e]	71	71[h]	76
Br	141[b]	163	22	268[e]	95	87[h]	92
Cl	141[b]	160	19	294[e]	121	103[h]	105
F	112[c]	151	39	369[f]	167	136[f]	133

[a] All data in kcal/mole at 298 °K.

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[g] Calculated using eq. 11 in text. IP(CH_3X) taken from e.

[h] Reference 10.

will be discussed: (1) The proton affinities of HI, HBr, and HCl are about the same, while PA(HF) is dramatically lower. (2) The methyl substituent effect on proton affinity, ΔPA in Table I, shows a marked reversal of trend between HCl and HF, and the effect for HF is very large.

The erratic behavior of the proton affinities of HX can be interpreted as resulting from the convolution of two opposite trends in the following sense. The hydrogen affinity of an ion M^+ is defined as the enthalpy change for reaction 10. It represents the homolytic bond

$$MH^+ \rightarrow M^+ + H \qquad (10)$$

dissociation energy of MH^+ and is related to the proton affinity of M by expression 11. In Table I are presented the ionization potentials of

$$PA(M) = HA(M^+) - IP(M) + IP(H) \qquad (11)$$

the hydrogen halides and the resultant $HA(HX^+)$ calculated with eq. 11. Both IP(HX) and $HA(HX^+)$ increase monotonically proceeding from iodine for fluorine. According to eq. 11, PA(HX) is related to the <u>difference</u> between $HA(HX^+)$ and IP(HX). Thus, the two progressions work in opposite directions and the approximately equal proton affinities of HI, HBr, and HCl result essentially from a cancellation effect. The exceptionally high ionization potential of HF, however, dominates $HA(HF^+)$ in expression 11, thus lowering PA(HF) drastically and accounting for the irregular sequence of HX proton affinities. Since $PA(CH_3X)$ exhibits a more orderly progression (Table I), this results in a very large methyl substituent effect for HF.[21]

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