ELSEVIER International Journal of Mass Spectrometry and Ion Processes 149/150 (1995) 543–553

International Journal of Mass Spectrometry and Ion Processes

Reactions of Fe^+ coordinated to the π-donating ligands C_2H_4, c-C_5H_5, C_6H_6 and C_{60} with N_2O and CO: probing the bonding in $(C_{60})Fe^+$[☆]

Vladimir Baranov, Diethard K. Bohme*

Department of Chemistry and Centre for Research in Earth and Space Science, York University, North York, Ont., Canada M3J 1P3

Received 2 May 1995; accepted 3 July 1995

Abstract

Experimental results are reported for gas-phase reactions of Fe^+ coordinated to the π-donating ligands C_2H_4, c-C_5H_5, C_6H_6 and C_{60} with N_2O and CO. Reaction rate coefficients and product distributions were measured with the selected-ion flow tube (SIFT) technique operating at 294 ± 3 K and a helium buffer gas pressure of 0.35 ± 0.01 Torr. The measurements provide intrinsic efficiencies for the primary and higher-order ligation of these XFe^+ cations with CO and N_2O and their corresponding coordination numbers. The coordination numbers are consistent with known ground state electronic structures. Many of the ligated ions were synthesized by ion/molecule ligation reactions in the gas phase for the first time, including $XFe(CO)_n^+$ and $XFe(N_2O)^+$ with X = C_2H_4, c-C_5H_5 and C_6H_6, $(C_{60})Fe(N_2O)^+$, $(C_{60})FeO^+$ and $(C_{60})FeO(N_2O)^+$. Also, the measurements provided an experimental assessment of the mode of bonding in $(C_{60})Fe^+$.

Keywords: Iron/fullerene cation; Ion/molecule reactions; Iron/cation reactivity; π-donating ligands; SIFT technique

1. Introduction

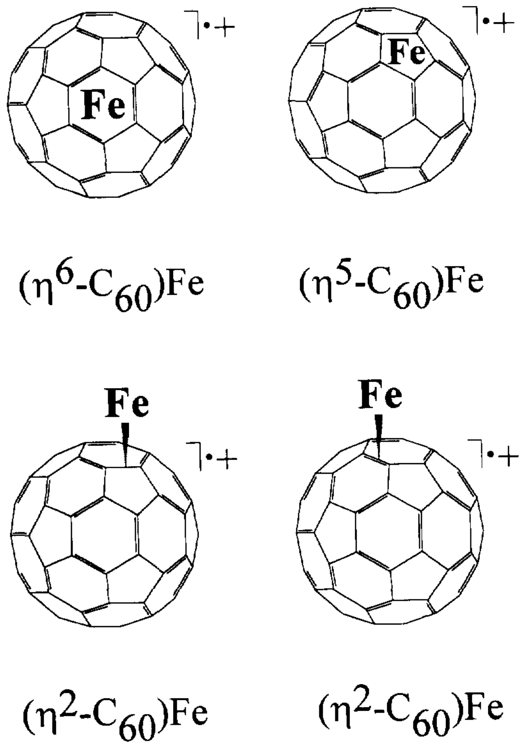
Our recent SIFT measurements of rate coefficients for the sequential ligation of FeO^+ with inorganic ligands in the gas phase under thermal equilibrium conditions have demonstrated that such measurements are useful in the determination of the coordination number of Fe^+ ligated with atomic oxygen [1]. Here we report measurements of rate coefficients and product distributions for the reactions of Fe^+ coordinated to the π-donating ligands C_2H_4, c-C_5H_5, C_6H_6 and C_{60}. N_2O and CO were chosen as the reactant neutrals. N_2O was chosen because of its general importance as an oxidizing agent and because our experience with FeO^+ had shown that this molecule is a well-behaved ligand. CO has long been of importance in fundamental studies of the ligation of XFe complexes both in the gas phase and the condensed phase. The purpose of this study was twofold. We were interested in exploring intrinsic kinetic features of the ligation of the π-coordinated Fe^+ with N_2O and CO. Secondly, we expected that an understanding of the ligation of XFe^+ (X = C_2H_4,

---

[☆] Dedicated to Professor David Smith FRS on the occasion of his 60th birthday.

* Corresponding author.

SSDI 0168-1176(95)04287-3



Scheme 1.

$c\text{-}C_5H_5$ and C_6H_6) with N_2O and CO would allow us to gain insight into the ligation of Fe^+ with C_{60}. Fe^+ can be envisaged to bond to C_{60} at three different sites on the carbon cage which strongly resemble the sites of bonding of Fe^+ to C_2H_4, $c\text{-}C_5H_5$ and C_6H_6. We hypothesized that a comparative study of the reactivities of Fe^+ ligated to all four of these ligands would identify the mode of bonding in $(C_{60})Fe^+$.

The modes of bonding of C_2H_4, $c\text{-}C_5H_5$ and C_6H_6 to Fe^+ are all different (η^2, η^5 and η^6, respectively) and should represent a complete set of possible modes of bonding with C_{60}. This is illustrated in Scheme 1. The electronic groundstates of $(C_2H_4)Fe^+$ ($^4B_2$) [2], $(c\text{-}C_5H_5)Fe^+$ ($^5E_2$) [3], and $(C_6H_6)Fe^+$ ($^4A_2$) [4] have recently all been characterized theoretically, together with their binding energies, which are 26, 77 ± 10 and 51 ± 5 kcal mol^{-1}, respectively. The computed binding energies compare favourably with the experimental values of 34 ± 2 [5], 88 ± 7 [6] and 55 ± 5 [7] kcal mol^{-1}, respectively, derived primarily from bracketing measurements using the FT-ICR technique. There has not been a reported computation for the binding energy of $(C_{60})Fe^+$, but a recent experimental study has suggested that C_{60} acts as a two-electron donor in $(C_{60})Fe^+$ [8]. Very recent bracketing measurements have led to a binding energy for this ligation of 44 ± 7 kcal mol^{-1} [9]. Theoretical [10] and experimental [11] studies of neutral $(C_{60})Fe$ suggest that, while bonding of iron to all of the reaction sites of C_{60} is possible, a strong preference is observed for the site between two adjacent six-membered rings.

2. Experimental

The results reported here were obtained using a selected-ion flow tube (SIFT) apparatus which has been described previously [12,13]. All measurements were performed at 294 ± 3 K and at a helium buffer gas pressure of 0.35 ± 0.01 Torr. The reactant Fe^+ and $(c\text{-}C_5H_5)Fe^+$ ions were generated directly from pure $(c\text{-}C_5H_5)_2Fe$ vapour, or a $(c\text{-}C_5H_5)_2Fe$ vapour/Ar mixture, in a low pressure ionization source by 50 eV electron-impact dissociative ionization. The ions were then mass selected, injected into the flow tube and allowed to thermalize by collisions (about 4×10^5) with He buffer gas atoms before entering the reaction region.

Assuming that the significant portion of the Fe^+ ions injected into the flow tube are in an excited state, and taking an He deactivation rate coefficient of 5×10^{-14} cm^3 $molecules^{-1}$ s^{-1} [14] (which corresponds to a deactivation time of about 4×10^{-3} s), one expects that the Fe^+ flow contains not more than 1% excited states at the beginning of the reaction region. Experimental evidence for the absence of excited states is provided by the linearity in the semilogarithmic decay of the Fe^+ signal observed over more than three orders of magnitude in the reactions with N_2O [1]. The presence of excited states with a reactivity different from that of the ground state would introduce curvature into the semilogarithmic decay.

$(C_2H_4)Fe^+$ and $(C_6H_6)Fe^+$ were produced from Fe^+ by association with ethylene and benzene which were introduced through the aspirator gas inlet (about 7×10^{16} and 1.1×10^{17} molecules s^{-1}, respectively) along with the helium buffer gas. We have found that the Fe^+ cation reacts relatively slowly with ethylene, $k_{obs} = (6.0 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The addition of a second molecule of C_2H_4 was observed to be approximately one order of magnitude faster than the primary reaction, $k_{obs} = (6.8 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. As a consequence, large amounts of Fe^+ were present when the $(C_2H_4)Fe^+$ ion signal was optimized (the measured ratio between the Fe^+ and $(C_2H_4)Fe^+$ ion intensities at the sampling orifice was about 10:1). However, this was not a problem in the measurements of the reactions of $(C_2H_4)Fe^+$ with CO and N_2O: Fe^+ does not react with CO and reacts with N_2O to produce FeO^+ which reacts with C_2H_4 to regenerate Fe^+. There is a mass coincidence between $(C_2H_4)Fe(CO)^+$ and the $(C_2H_4)_2Fe^+$ initially present (see Fig. 1). The association reaction between Fe^+ and C_6H_6 was observed to be quite rapid, $k_{obs} = (7.8 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

$C_{60}Fe^+$ was produced by the association reaction of Fe^+ with C_{60}. The C_{60} vapour, obtained from a heated fullerene sample (97% C_{60}, approx. 2% C_{70}), was introduced into the flow tube upstream of the reaction region via a heated stainless steel shielded inlet. This inlet allowed the flow of the C_{60} vapour to be varied, but not to be measured. A small, but insignificant, increase in temperature of the helium buffer gas (from 294 to 305 K) was observed with a thermocouple at the entrance of the reaction region. Under these conditions Fe^+ was observed to react with C_{60} by electron transfer to produce C_{60}^+ and by association to produce $C_{60}Fe^+$ in a ratio of about 1:3. The $C_{60}Fe^+$ formed in this way was allowed to thermalize for about 7 ms (about 10^5 collisions with He buffer gas atoms) before reaction further downstream. The C_{60}^+ did not react with N_2O and CO, $k < 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

N_2O and CO were introduced into the reaction region as pure gases. All neutral reagents were obtained commercially and were of high purity (generally >99%). The rate coefficients for primary reactions reported here are estimated to have an absolute accuracy of ±30%.

3. Results and discussion

3.1. Reactions with CO

While Fe^+ was observed not to react measurably with CO under our SIFT conditions, $k < 1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, ligation of Fe^+ with C_2H_4, $c\text{-}C_5H_5$, C_6H_6 and C_{60} dramatically increased the measured reactivity, $k > 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (see Table 1). Furthermore, sequential addition of CO was observed, but to varying degrees: two molecules were detected to add to $(C_6H_6)Fe^+$, three to $(c\text{-}C_5H_5)Fe^+$, and four to $(C_2H_4)Fe^+$ and $(C_{60})Fe^+$ according to reactions (1)–(4):

$$(C_2H_4)Fe(CO)_{n-1}^+ + CO \rightarrow (C_2H_4)Fe(CO)_n^+ \quad \text{where } n = 1\text{–}4 \tag{1}$$

$$(c\text{-}C_5H_5)Fe(CO)_{n-1}^+ + CO \rightarrow (c\text{-}C_5H_5)Fe(CO)_n^+ \quad \text{where } n = 1\text{–}3 \tag{2}$$

$$(C_6H_6)Fe(CO)_{n-1}^+ + CO \rightarrow (C_6H_6)Fe(CO)_n^+ \quad \text{where } n = 1, 2 \tag{3}$$

Table 1
Results for SIFT measurements of the reactions of Fe^+ and XFe^+ cations with CO and N_2O at 294 ± 3 K in helium buffer gas at a total pressure of 0.35 ± 0.01 Torr for X = c-C_5H_5, C_6H_6, C_2H_4 and C_{60}

Cation XFe^+	CO		N_2O			
	k_{obs}[a] (k_{cap})[b]	$XFe(CO)_n^+$, n[c]	k_{obs}[a] (k_{cap})[b]	$XFe(N_2O)^+$	$XFeO^+$	$XFeO(N_2O)^+$
Fe^+	<0.0001[d] (7.6)	NR[e]	0.31 ± 0.01[d] (8.6)		[1][f]	+[g]
$(C_2H_4)Fe^+$	0.54 ± 0.02 (7.4)	4	1.2 ± 0.1 (7.9)	[0.08]	[0.92]	+
$(c\text{-}C_5H_5)Fe^+$	1.1 ± 0.1 (7.1)	3	2.5 ± 0.1 (7.5)	[1]		–
$(C_6H_6)Fe^+$	2.7 ± 0.4 (7.0)	2	3.3 ± 0.3 (7.4)	[0.32]	[0.68]	–
$(C_{60})Fe^+$	1.3 ± 0.1 (6.5)	4	1.7 ± 0.2 (6.6)	[0.41]	[0.59]	+

[a] Observed effective bimolecular reaction rate coefficient, expressed in units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}.
[b] Collision rate coefficient is given in parentheses and calculated according to the ADO method [17] and expressed in the same units as k_{obs}.
[c] n, number of the CO ligands in the terminal product cation.
[d] The values for the rate coefficients for reactions of Fe^+ with CO and N_2O were previously reported in Ref. [1].
[e] No reaction observed.
[f] Branching ratios are given in square brackets and are accurate to ±10%.
[g] + designates the observation of adduct formation; – designates the failure to observe adduct formation.

$$C_{60}Fe(CO)_{n-1}^+ + CO \rightarrow C_{60}Fe(CO)_n^+ \quad \text{where } n = 1\text{–}4 \qquad (4)$$

Representative experimental results for the sequential addition of CO to XFe^+ are shown in Figs. 1–4 for X = C_2H_4, c-C_5H_5, C_6H_6 and C_{60}, respectively. Reactions (1)–(4) are presumed to occur, under our operating conditions, by termolecular association with the He buffer gas atoms acting as the stabilizing third body.

For reactions (1) our mass spectrometer could not rule out the occurrence of switching reactions with CO leading to the conversion of $(C_2H_4)Fe(CO)_{n-1}^+$ to $Fe(CO)_n^+$. However, previous ICR measurements with C_2D_4 have shown that this conversion occurs in the reverse direction [15].

3.2. Reactions with N_2O

The chemistry observed with N_2O was quite different from that observed with CO. Adduct formation, while again proceeding with measurable efficiency, was observed to compete with O atom abstraction according to reactions (5a) and (5b):

$$XFe^+ + N_2O \rightarrow XFe(N_2O)^+ \qquad (5a)$$

$$\rightarrow XFeO^+ + N_2 \qquad (5b)$$

Secondary association reactions with N_2O of type (6)

$$XFeO(L)_{n-1}^+ + L \rightarrow XFeO(L)_n^+ \qquad (6)$$

were observed to lead to the ligation of $XFeO^+$ to varying degrees depending on the nature of X. We have reported elsewhere that FeO^+ reacts with nitrous oxide and sequentially forms the ligated FeO^+ cations $FeO(N_2O)_n^+$ with n = 1, 2 and 3 [1].

The chemistry initiated by $(C_2H_4)Fe^+$ with N_2O is shown in Fig. 5 and can be described by reactions (7a) and (7b):

$$(C_2H_4)Fe^+ + N_2O \rightarrow (C_2H_4)Fe(N_2O)^+ \qquad (7a)$$

$$\rightarrow (C_2H_4)FeO^+ + N_2 \qquad (7b)$$

The branching ratio k_{7a}/k_{7b} was measured to be 0.08/0.92. Reaction (7b) was followed by

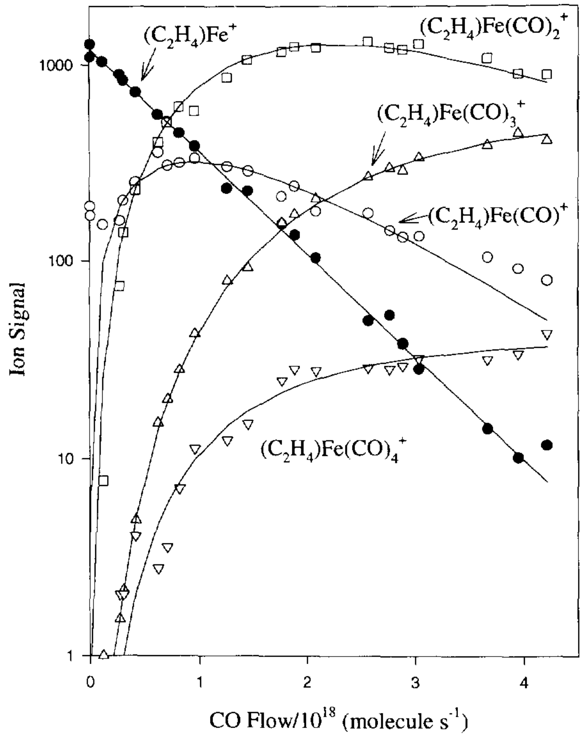


Fig. 1. Experimental data for the reaction of (C$_2$H$_4$)Fe$^+$ with CO. The solid lines represent a fit of the experimental data with the solution of the system of differential equations appropriate for the observed sequential reactions. The fifth adduct (C$_2$H$_4$)Fe(CO)$_5^+$ could not be detected.

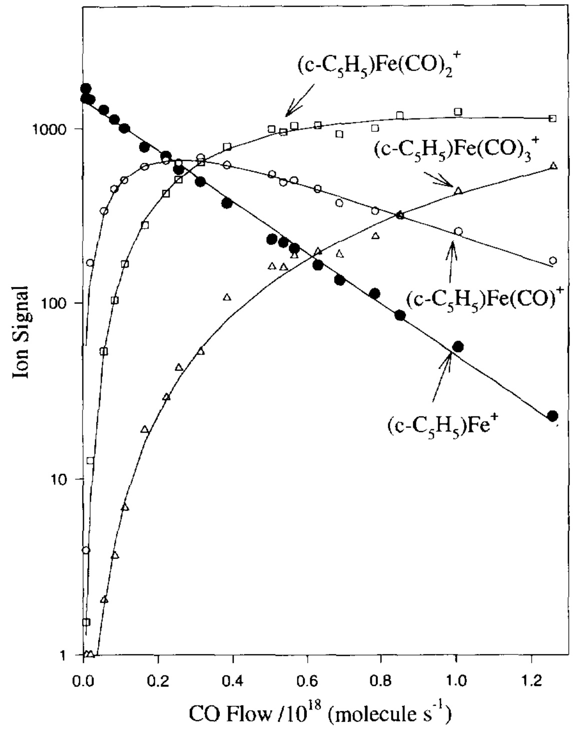


Fig. 2. Experimental data for the reaction of (c-C$_5$H$_5$)Fe$^+$ with CO. The solid lines represent a fit of the experimental data with the solution of the system of differential equations appropriate for the observed sequential reactions. The fourth adduct (c-C$_5$H$_5$)Fe(CO)$_4^+$ could not be detected.

the addition reaction

$$(C_2H_4)FeO^+ + N_2O \rightarrow (C_2H_4)FeO(N_2O)^+ \qquad (8)$$

$k_8 = (7.0 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

It is also important to note that the (C$_2$H$_4$)FeO(N$_2$O)$^+$ cation was observed to add one more N$_2$O ligand, but at a very slow rate under our experimental conditions. Curve fitting indicated that second addition of N$_2$O is approximately two orders of magnitude slower than reaction (8). Tertiary adduct formation was not detectable ($k < 5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}).

(C$_2$H$_4$)$_2$Fe$^+$ also was observed to react with N$_2$O. The products of this reaction could not be fully characterized because of low signal intensities, but formation of (C$_2$H$_4$)$_2$FeO$^+$ was observed.

Experimental results for the reaction of (c-C$_5$H$_5$)Fe$^+$ with N$_2$O are shown in Fig. 6 and correspond to the addition reaction

$$(c\text{-}C_5H_5)Fe^+ + N_2O \rightarrow (c\text{-}C_5H_5)Fe(N_2O)^+ \qquad (9)$$

There was no evidence in this case for secondary adduct formation or the oxidation of iron to form (c-C$_5$H$_5$)FeO$^+$, $k_{10} < 5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}:

$$(c\text{-}C_5H_5)Fe(N_2O)^+ + N_2O \rightarrow \text{no reaction} \qquad (10)$$

The absence of the secondary processes and

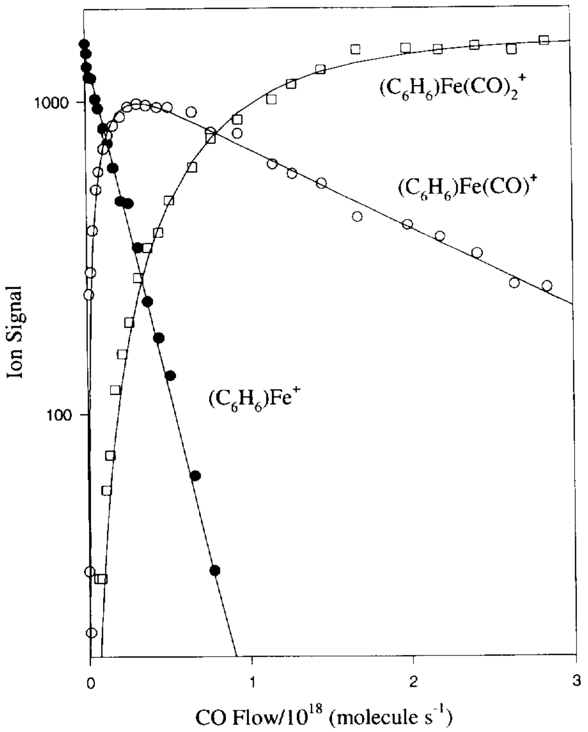


Fig. 3. Experimental data for the reaction of $(C_6H_6)Fe^+$ with CO. The solid lines represent a fit of the experimental data with the solution of the system of differential equations appropriate for the observed sequential reactions. The third adduct $(C_6H_6)Fe(CO)_3^+$ could not be detected.

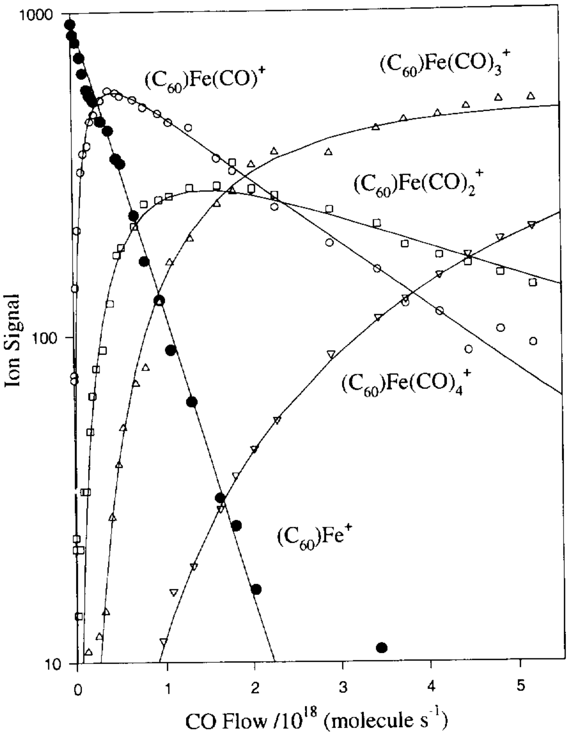


Fig. 4. Experimental data for the reaction of $(C_{60})Fe^+$ with CO. The solid lines represent a fit of the experimental data with the solution of the system of differential equations appropriate for the observed sequential reactions. The fifth adduct $(C_{60})Fe(CO)_5^+$ could not be detected.

the oxidation reaction (5b) in this case sharply distinguishes the reactivity of $(c\text{-}C_5H_5)Fe^+$ toward N_2O from that of all the other XFe^+ cations investigated in this study.

Observed parent and product ion intensities versus molecular flow of N_2O for the reaction of $(C_6H_6)Fe^+$ with N_2O are shown in Fig. 7. The primary decay of $(C_6H_6)Fe^+$ provides a rate coefficient of $(3.3 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and corresponds to the occurrence of the following association reaction and oxidation:

$$(C_6H_6)Fe^+ + N_2O \rightarrow (C_6H_6)Fe(N_2O)^+ \quad (11a)$$

$$\rightarrow (C_6H_6)FeO^+ + N_2 \quad (11b)$$

In this case the branching ratio k_{11a}/k_{11b} was measured to be 0.32:0.68. The $(C_6H_6)Fe(N_2O)^+$ and $(C_6H_6)FeO^+$ cations did not react further, $k < 5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. A recent FT-ICR study of the reaction of $(C_6H_6)Fe^+$ with N_2O has led to results different from those obtained here with the SIFT instrument [16]. The reported FT-ICR rate coefficient has a value of 8.4×10^{-10} cm^3 molecule^{-1} s^{-1}, which is 2.5 times larger than our value. Also the observed products in the FT-ICR measurements are different: adduct formation (channel (11a)) was not seen but N_2 elimination (channel (11b)) was also observed as the major channel. The two minor channels leading to $(C_5H_6)Fe^+$ and $(C_6H_4)FeO^+$ formation which were seen in the FT-ICR experiments were absent in our SIFT experiments. These differences can be explained, in

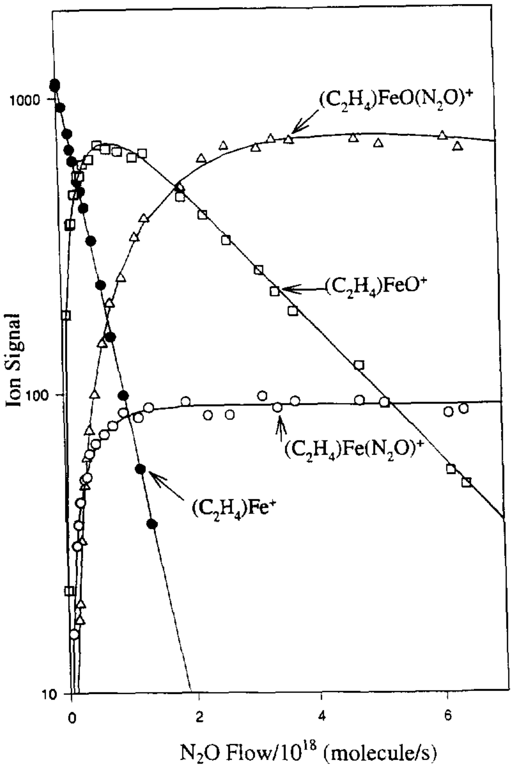


Fig. 5. Experimental data for the reaction of $(C_2H_4)Fe^+$ with N_2O. The solid lines represent a fit of the experimental data with the solution of the system of differential equations appropriate for the observed sequential reactions. The low intensity ions $(C_2H_4)_2FeO^+$ and $(C_2H_4)FeO(N_2O)_2^+$ evident at higher flows have not been plotted for simplicity but were detected.

part, in terms of the different pressures in the two instruments. Under our SIFT conditions, collisional stabilization is much more effective.

Experimental results for the reaction of $C_{60}Fe^+$ with N_2O are shown in Fig. 8. Oxidation was also observed to compete with ligation in this reaction:

$$(C_{60})Fe^+ + N_2O \rightarrow (C_{60})Fe(N_2O)^+ \qquad (12a)$$

$$\rightarrow (C_{60})FeO^+ + N_2 \qquad (12b)$$

The branching ratio k_{12a}/k_{12b} was measured to be 0.41 : 0.59, and following addition:

$$(C_{60})FeO^+ + N_2O \rightarrow (C_{60})FeO(N_2O)^+ \qquad (13)$$

There is no evidence to suggest the presence of $(C_{60})FeO(N_2O)_2^+$ under our experimental conditions, $k_{obs} < 5 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹.

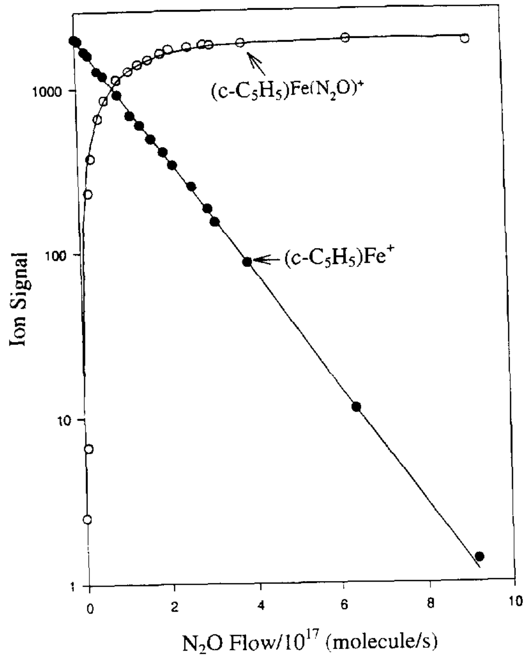


Fig. 6. Experimental data for the reaction of $(c\text{-}C_5H_5)Fe^+$ with N_2O. The solid lines represent a fit of the experimental data with the solution of the system of differential equations appropriate for the observed sequential reactions.

3.3. The influence of ligation on the reactivity of Fe^+

The observed reactivity of Fe^+ coordinated to π-electron-donating ligands affords important insight into the bonding properties of these ions: information about the coordination number of iron in the higher-order ligated species $XFe(CO)_n^+$ and $XFeO(N_2O)_n^+$ and thus information about the mode of coordination. Also, the kinetic measurements provide a measure of intrinsic reaction efficiencies of ligation. We define reaction efficiency, *Eff*, in the usual way as the ratio of the observed rate coefficient to the capture rate coefficient calculated by ADO collision theory [17], k_{obs}/k_{cap}.

The efficiency of the ligation of XFe^+ with CO observed under our operating conditions was in the range from 0.073 to 0.39, in sharp contrast with the ligation of bare Fe^+ which was not observed, $Eff < 10^{-5}$. The failure to

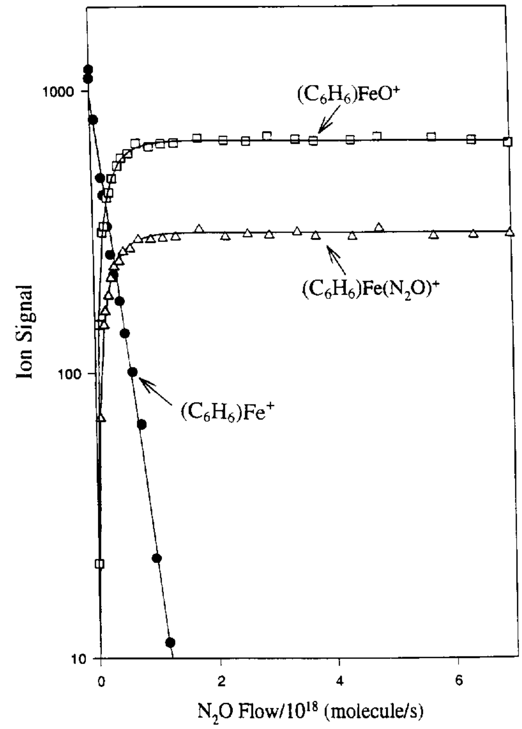


Fig. 7. Experimental data for the reaction of $(C_6H_6)Fe^+$ with N_2O. The solid lines represent a fit of the experimental data with the solution of the system of differential equations appropriate for the observed sequential reactions.

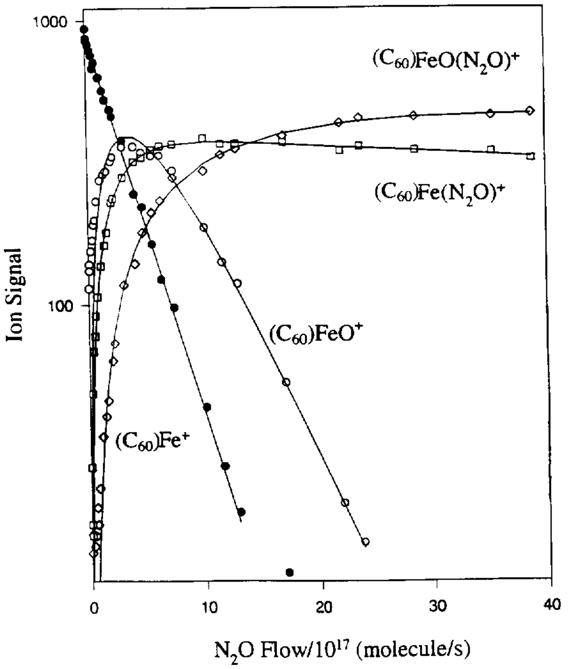


Fig. 8. Experimental data for the reaction of $(C_{60})Fe^+$ with N_2O. The solid lines represent a fit of the experimental data with the solution of the system of differential equations appropriate for the observed sequential reactions. The second adduct $(C_{60})FeO(N_2O)_2^+$ could not be detected.

observe addition of CO to Fe^+ is unexpected, given the relatively high binding energy of CO to Fe^+, 31.3 ± 1.8 kcal mol^{-1} [18], in spite of the small number of degrees of freedom in the intermediate complex available for energy dispersal. However, we also note that a comparison of the electronic structures of bare Fe^+ and XFe^+ shows that Fe^+ is unique: the spatially extended 4s orbital is singly occupied in the ^6D ground state ($4s^1 3d^6$) of Fe^+ which contributes to the repulsive interaction between the electron in the 4s orbital of Fe^+ and the σ-donor orbital of the CO ligand. So we expect that the $Fe^+(^6D)$–CO complex has a lifetime against unimolecular decomposition which is shorter than the time required for the conversion to the $FeCO^+$ quartet state [19] and its collisional stabilization. A similar interaction is absent in the electronic ground states of $(C_5H_5)Fe^+$ ($^5E_2$) [3] and $(C_6H_6)Fe^+$ ($^4A_2$) [4] and, since the $3d\sigma$ orbital is much smaller than the 4s orbital, there is less repulsive interaction with the CO ligands. We believe that the electronic ground state of $(C_{60})Fe^+$ is also a quartet.

The observed trend in ligation efficiency with CO, $Eff_{CO}[(C_6H_6)Fe^+] = 0.39 > Eff_{CO}[(c\text{-}C_5H_5)Fe^+] = 0.15 > Eff_{CO}[(C_2H_4)Fe^+] = 0.073$, parallels the trend in the number of degrees of freedom that may be effective in the energy dispersal in the intermediate XFe^+–CO complex. The one apparent exception is the $Eff_{CO}[(C_{60})Fe^+] = 0.2$, which falls between $Eff_{CO}[(C_6H_6)Fe^+]$ and $Eff_{CO}[(C_5H_5)Fe^+]$. This implies that C_{60} is less involved in energy dispersal than C_6H_6 or $c\text{-}C_5H_5$. However, it should be noted that the ADO collision theory is least appropriate for the reaction of $(C_{60})Fe^+$ with CO since $(C_{60})Fe^+$ can hardly be considered as a point charge. Also steric shielding of Fe^+ by the large C_{60} ligand may play a role in determining reaction efficiency.

The observations that two molecules of CO add to $(C_6H_6)Fe^+$, three to $(c\text{-}C_5H_5)Fe^+$, and four to $(C_2H_4)Fe^+$ and $C_{60}Fe^+$ according to reactions (1)–(4) are consistent with Tolman's 18-electron rule and can be attributed to the completion or saturation of the electron shell of iron ($(c\text{-}C_5H_5)Fe(CO)_3^+$—18 electrons; $(C_6H_6)Fe(CO)_2^+$, $(C_2H_4)Fe(CO)_4^+$ and most probably also $C_{60}Fe(CO)_4^+$—the 17 electron species). Analogous compounds have been identified in the condensed phase ($c\text{-}C_5H_5Fe(CO)_2Cl$ (or $(c\text{-}C_5H_5)Mn(CO)_3$ which is isoelectronic with $(c\text{-}C_5H_5)Fe(CO)_3^+$) [20], and $C_{60}Fe(CO)_4$ [11].

The trend in ligation efficiency observed with N_2O is quite different from that observed with CO. The efficiency of $XFe(N_2O)^+$ formation is highest with $(C_5H_5)Fe^+$ for which a competing O-atom abstraction channel was absent. For the other adduct formation reactions which compete with O-atom abstraction, the order of ligation efficiency is $Eff_{N_2O}[(C_6H_6)Fe^+] = 0.15 > Eff_{N_2O}[(C_{60})Fe^+] = 0.1 > Eff_{N_2O}[(C_2H_4)Fe^+] = 0.012 > Eff_{N_2O}[Fe^+] < 10^{-5}$, which is in accord with a decrease in the number of degrees of freedom effective in the energy dispersal. The highest efficiency for O-atom abstraction belongs to $(C_6H_6)Fe^+$ and the lowest to bare Fe^+. The reasons for the low efficiency of the reaction with Fe^+ have been discussed elsewhere [1]. The order of efficiency for the overall reaction (5a) + (5b) is $Eff_{N_2O}[(C_6H_6)Fe^+] = 0.45 > Eff_{N_2O}(c\text{-}C_5H_5)Fe^+] = 0.3 > Eff_{N_2O}[(C_{60})Fe^+] = 0.26 > Eff_{N_2O}[(C_2H_4)Fe^+] = 0.15 > Eff_{N_2O}[Fe^+] = 0.036$.

The occurrence of O-atom abstraction in reaction (5b) is perhaps not surprising since the O-atom affinity of N_2 is quite low, 40 kcal mol^{-1}, much lower than that of C, 257.3 kcal mol^{-1} [21]. Fe^+ was observed to react exclusively by O-atom transfer, $k = 3.1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. The absence of O-atom abstraction in the reaction of $(c\text{-}C_5H_5)Fe^+$ with N_2O markedly differs from all the other XFe^+ systems investigated. This may be attributed to the unfavorable increase, up to 4, in the formal oxidation number of iron which would be required in the formation of the $(c\text{-}C_5H_5)Fe^+\text{–}O$ bond.

The observed pattern of addition of N_2O to XFe^+ and $XFeO^+$ can be rationalized in terms of electronic structure considerations. Our results suggest that $(C_2H_4)FeO^+$ has the same multiplicity as FeO^+ and that π back donation from C_2H_4 occurs into empty Fe^+ orbitals. The back donation of the π-electrons from C_2H_4 and the electron pair from O to 4s and 4p orbitals of Fe^+ allows two orbitals to be available for N_2O coordination. A similar explanation can account for the observed ligation of the electronic ground states of $FeO^+(^6\Sigma^+)$ [22] and $(c\text{-}C_5H_5)Fe^+$ $(^5E_2)$ [3]. Assuming that the observed $FeO(N_2O)_n^+$ (with $n = 0\text{–}3$) cations have the same multiplicity, one may conclude that back donation from O to the Fe cation leaves three orbitals available for the coordination of N_2O ligands. In the case of $(c\text{-}C_5H_5)Fe^+$ the back donation of the π-electrons from $(c\text{-}C_5H_5)^-$ to the Fe^{2+} cation leaves only one orbital available for donation of the N_2O lone electron pair. From this point of view $FeO(N_2O)_3^+$ and $(c\text{-}C_5H_5)Fe(N_2O)^+$ are coordinatively saturated cations and are unable to add more ligands. We also believe that $(C_6H_6)Fe(N_2O)^+$ and $(C_6H_6)FeO^+$ are coordinatively saturated complexes and cannot react further with N_2O. The back donation of the π-electrons from (C_6H_6) to 4s and 4p orbitals of Fe^+ leaves only one orbital available for donation of the N_2O lone electron pair. The electronic structure of $(C_6H_6)FeO^+$ is unknown. However, if the multiplicity is equal to 6 (in analogy with FeO^+), back donation of the π-electrons from (C_6H_6) and the electron pair from O to the 4s and 4p orbitals of Fe^+ can form a coordinatively saturated complex.

3.4. The bonding in $(C_{60})Fe^+$

Can we find a reasonably good match between the reactivity of $(C_{60})Fe^+$ and the reactivities of the other XFe^+ complexes observed in this study? A striking feature of the results in Table 1 and Figs. 1–4 is that, of the five iron-containing ions investigated, only $(C_2H_4)Fe^+$ and $(C_{60})Fe^+$ are able to add up to four CO ligands. This result implies that the site of bonding of Fe in $(C_{60})Fe^+$ has an electronic structure close to or isoelectronic with that in $(C_2H_4)Fe^+$. Sequential CO addition to these cations is expected to reduce spin multiplicity; the 17-electron species $(C_2H_4)Fe(CO)_4^+$ and $C_{60}Fe(CO)_4^+$ should both have doublet ground states.

The match in the reactivities of $(C_2H_4)Fe^+$ and $(C_{60})Fe^+$ also appears in the reactivities with N_2O. Both react with N_2O by adduct formation and oxidation, although the branching ratio for adduct formation is much higher in the case of $(C_{60})Fe^+$. Also, the secondary N_2O chemistry reveals that only iron ligated to C_2H_4 and C_{60} forms $XFeO(N_2O)^+$ complexes. There is, however, a difference in the tertiary reactions with N_2O: $(C_{60})FeO(N_2O)^+$ was observed not to react further with N_2O with a measurable rate while addition to $(C_2H_4)FeO(N_2O)^+$ was clearly observed, albeit with a rate significantly slower than that of the previous step. This difference in reactivity may be attributed to the steric availability of a free coordination site around iron which is expected to decrease more with higher-order additions in the presence of a big C_{60} co-ligand.

The match in reactivity with CO and N_2O between $(C_2H_4)Fe^+$ and $(C_{60})Fe^+$ suggests an electron-donating ability for C_{60} similar to that for C_2H_4. This result is in good agreement with recently reported FT-ICR results [8] which suggest that C_{60} as a two-electron donor in gas-phase organometallic ions $(C_{60})M^+$. Thus, it appears that all possible modes of C_{60} coordination to Fe^+ (see Scheme 1) can be ruled out except for $(\eta^2\text{-}C_{60})Fe^+$ and that the gas phase complexes of iron coordinated to C_{60} which were synthesized in this study can be written as $(\eta^2\text{-}C_{60})FeO^+$, $(\eta^2\text{-}C_{60})FeO(N_2O)^+$ and $(\eta^2\text{-}C_{60})Fe(CO)_n^+$, where $n = 1$, 2 and 3.

4. Conclusions

Reactivities have been measured for the π-coordinated iron cations $(C_2H_4)Fe^+$, $(c\text{-}C_5H_5)Fe^+$, $(C_6H_6)Fe^+$ and $(C_{60})Fe^+$ with CO and N_2O at 294 ± 2 K in helium buffer gas at a total pressure of 0.35 ± 0.01 Torr. They provide a measure of intrinsic efficiencies for the primary and higher-order ligation of these XFe^+ cations with CO and N_2O and their corresponding coordination numbers. The coordination numbers are consistent with known ground state electronic structures. Many of the ligated ions were synthesized by ion/molecule ligation reactions in the gas phase for the first time, including $XFe(CO)_n^+$ and $XFe(N_2O)^+$ with $X = C_2H_4$, $c\text{-}C_5H_5$ and C_6H_6, $(C_{60})Fe\ (N_2O)^+$, $(C_{60})FeO^+$ and $(C_{60})FeO(N_2O)^+$. Also, the measurements provided an experimental assessment of the mode of bonding in $(C_{60})Fe^+$.

Acknowledgement

D.K.B. is grateful to the Natural Sciences and Engineering Research Council of Canada for the financial support of this research.

References

[1] V.I. Baranov, G. Javahery, A.C. Hopkinson and D.K. Bohme, J. Am. Chem. Soc., 1995, submitted for publication.
[2] M. Sodupe, C.W. Bauschlicher, Jr., S.R. Langhoff and H. Partridge, J. Phys. Chem., 96 (1992) 2118.
[3] M. Sodupe and C.W. Bauschlicher, Jr., Chem. Phys. Lett., 207 (1993) 19.
[4] C.W. Bauschlicher, Jr., H. Partridge and S.R. Langhoff, J. Phys. Chem., 96 (1992) 3273.
[5] D.B. Jacobson and B.S. Freiser, J. Am. Chem. Soc., 105 (1983) 7492.
[6] Y. Huang and B.S. Freiser, J. Am. Chem. Soc., 112 (1990) 5085.
[7] R.L. Hettich, T.C. Jackson, E.M. Stanko and B.S. Freiser, J. Am. Chem. Soc., 108 (1986) 5086.
[8] Q. Jiao, Y. Huang, S.A. Lee, J.R. Gord and B.S. Freiser, J. Am. Chem. Soc., 114 (1992) 2726.
[9] S.Z. Kan, Y.G. Byun, S.A. Lee and B.S. Freiser, J. Mass Spectrom., 30 (1995) 194.
[10] F. Chen, D. Singh and S.A. Jansen, J. Phys. Chem., 97 (1993) 10958.
[11] R.E. Douthwaite, M.L.H. Green, A.H.H. Stephens and J.F.C. Turner, J. Chem. Soc., Chem. Commun., (1993) 1522.
[12] G.I. Mackay, G.D. Vlachos, D.K. Bohme and H.I. Schiff, Int. J. Mass Spectrom. Ion Phys., 36 (1980) 259.
[13] A.B. Raksit and D.K. Bohme, Int. J. Mass Spectrom. Ion Processes, 55 (1983) 69.
[14] P.R. Kemper and M.T. Bowers, J. Phys. Chem., 95 (1991) 5134.
[15] M.S. Foster and J.L. Beauchamp, J. Am. Chem. Soc., 97 (1975) 4808.
[16] D. Stöckigt and H. Schwarz, Chem. Ber., 127 (1994) 2499.
[17] T. Su and M.T. Bowers, Int. J. Mass. Spectrom. Ion Phys., 12 (1973) 347.
[18] R.H. Schultz, K.C. Crellin and P.B. Armentrout, J. Am. Chem. Soc., 113 (1991) 8590.
[19] L.A. Barnes, M. Rosi and C.W. Bauschlicher, Jr., J. Chem. Phys., 93 (1990) 609.
[20] F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry: A Comprehensive Text, 5th edn., New York, Wiley-Interscience, 1988, p. 78.
[21] S. Wlodek and D.K. Bohme, J. Chem. Soc., Faraday Trans., 85 (1989) 1643.
[22] A. Fiedler, J. Hrusak, W. Koch and H. Schwarz, Chem. Phys. Lett., 211 (1993) 242.