Coordination chemistry of Fe^+, $(c\text{-}C_5H_5)Fe^+$, and $(c\text{-}C_5H_5)_2Fe^+$ in the gas phase at room temperature: kinetics of sequential ligation with hydrogen cyanide and cyanoacetylene

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Abstract

Measurements with the selected-ion flow tube technique are reported for the room-temperature kinetics of the sequential ligation of Fe^+ and $(c\text{-}C_5H_5)Fe^+$ with HCN and HC_3N in helium bath gas at 0.35 Torr. $(c\text{-}C_5H_5)_2Fe^+$ was observed not to react. Titration curves of the variation in the apparent bimolecular rate coefficient for ligation with the number of ligands provide cyanide coordination numbers for Fe^+ in the absence (4) and presence (3) of $c\text{-}C_5H_5$. Multicollision induced dissociation experiments indicate the absence of intramolecular ligand–ligand interaction mediated by Fe^+. (Int J Mass Spectrom 210/211 (2001) 303–310) © 2001 Elsevier Science B.V.

Keywords: Fe^+; $(c\text{-}C_5H_5)Fe^+$; hydrogen cyanide; cyanoacetylene; gas-phase ligation kinetics; SIFT technique; CID technique

1. Introduction

It is now well established that intrinsic kinetic and thermodynamic features of ligation reactions involving organometallic ions of the type known to occur in solution can be scrutinized and measured in the gas phase. In our laboratory we have found that flow-tube mass spectrometry, in which bare and ligated ions are generated in a region spatially separated from the reaction region, is ideally suited for such investigations. Rate coefficients for sequential ligation reactions of type

$$ML_n^+ + L + He \rightarrow ML_{n+1}^+ + He \qquad (1)$$
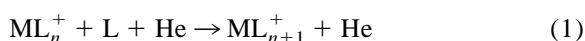
proceeding at room temperature in He bath gas (at 0.35 Torr) can be measured and these provide insight into the intrinsic efficiency of ligation. The helium bath gas has a sufficiently high density to bring about collisional stabilization of the ligated product ion. A measure of the intrinsic co-ordination number of the core ion becomes available when ligand saturation is observed. In our laboratory the ligation studies are augmented by subjecting the ligated ions produced in reaction (1) to multicollision induced dissociation and measuring their dissociation thresholds. Such measurements provide relative binding energies and insights into the occurrence of intramolecular ligand–ligand interactions by revealing bond connectivities in the ligated ions.

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Dedicated to Professor Nico M.M. Nibbering on the occasion of his retirement and for his many splendid contributions over the years to the field of gas-phase ion chemistry.

Table 1

Measured products and rate coefficients for reactions initiated by ground-state Fe^+ and $(c\text{-}C_5H_5)Fe^+$ cations with HCN and HC_3N at 294 ± 3 K in helium buffer gas at a total pressure of 0.35 ± 0.01 Torr; reaction[a] and collision[b] rate coefficients are given in units of cm^3 molecules^{-1} s^{-1}

| Reactant molecule	Reactant/product ions[c]	k_{exp}	k_c	k_{exp}/k_c
HCN	$Fe^+/Fe^+(HCN)$	1.5×10^{-11}	3.3×10^{-9}	4.5×10^{-3}
	$Fe^+(HCN)/Fe^+(HCN)_2$	3.6×10^{-10}	3.1×10^{-9}	0.12
	$Fe^+(HCN)_2/Fe^+(HCN)_3$	$(5\pm2) \times 10^{-10}$	3.0×10^{-9}	0.17
	$Fe^+(HCN)_3/Fe^+(HCN)_4$	$(3\pm2) \times 10^{-10}$	2.9×10^{-9}	0.10
	$Fe^+(HCN)_4/Fe^+(HCN)_5$	$<10^{-12}$	2.9×10^{-9}	$<3.4 \times 10^{-4}$
	$(c\text{-}C_5H_5)Fe^+/ (c\text{-}C_5H_5)Fe^+(HCN)$	2.9×10^{-9}	3.0×10^{-9}	1.0
	$(c\text{-}C_5H_5)Fe^+(HCN)/(c\text{-}C_5H_5)Fe^+(HCN)_2$	7.8×10^{-10}	2.9×10^{-9}	0.27
	$(c\text{-}C_5H_5)Fe^+(HCN)_2/ (c\text{-}C_5H_5)Fe^+(HCN)_3$	6.3×10^{-11}	2.9×10^{-9}	2.2×10^{-2}
	$(c\text{-}C_5H_5)Fe^+(HCN)_3/(c\text{-}C_5H_5)Fe^+(HCN)_4$	$<10^{-12}$	2.9×10^{-9}	$<3.4 \times 10^{-4}$
	$(c\text{-}C_5H_5)_2Fe^+/ (c\text{-}C_5H_5)_2Fe^+ (HCN)$	$<1 \times 10^{-13}$	2.9×10^{-9}	$<3.4 \times 10^{-5}$
HC_3N	$Fe^+/Fe^+(HC_3N)$	4.2×10^{-10}	3.4×10^{-9}	0.12
	$Fe^+(HC_3N)/Fe^+(HC_3N)_2$	6.4×10^{-10}	3.0×10^{-9}	0.21
	$Fe^+(HC_3N)_2/Fe^+(HC_3N)_3$	6.9×10^{-10}	2.9×10^{-9}	0.24
	$Fe^+(HC_3N)_3/Fe^+(HC_3N)_4$	7.8×10^{-10}	2.8×10^{-9}	0.28
	$Fe^+(HC_3N)_4/Fe^+(HC_3N)_5$	$<10^{-12}$	2.7×10^{-9}	$<3.7 \times 10^{-4}$
	$(c\text{-}C_5H_5)Fe^+/ (c\text{-}C_5H_5)Fe^+ (HC_3N)$	2.8×10^{-9}	3.0×10^{-9}	0.93
	$(c\text{-}C_5H_5)Fe^+(HC_3N)/ (c\text{-}C_5H_5)Fe^+(HC_3N)_2$	2.2×10^{-9}	2.8×10^{-9}	0.79
	$(c\text{-}C_5H_5)Fe^+(HC_3N)_2/ (c\text{-}C_5H_5)Fe^+(HC_3N)_3$	1.5×10^{-9}	2.8×10^{-9}	0.54
	$(c\text{-}C_5H_5)Fe^+(HC_3N)_3/ (c\text{-}C_5H_5)Fe^+(HC_3N)_4$	$<10^{-12}$	2.7×10^{-9}	$<3.7 \times 10^{-4}$
	$(c\text{-}C_5H_5)_2Fe^+/ (c\text{-}C_5H_5)_2Fe^+(HC_3N)$	$<1 \times 10^{-13}$	2.8×10^{-9}	$<3.6 \times 10^{-5}$

[a] Uncertainty in the reaction rate coefficient is less than 30%, unless indicated otherwise.

[b] Collision rate coefficient is calculated according to the algorithm of the combined variational transition-state theory developed by Su and Chesnavich [20].

We have previously surveyed intrinsic features of the kinetics of ion ligation for FeO^+ [1–3], Fe^+ [1,4–6], $(c\text{-}C_5H_5)Fe^+$, and $(c\text{-}C_5H_5)_2Fe^+$ cations [2,5,6] as well as Mg^+ [5,7,8], $(c\text{-}C_5H_5)Mg^+$, and $(c\text{-}C_5H_5)_2Mg^+$ cations [7,8]. Ligands that we have investigated include the inorganic ligands H_2, HD, D_2, NH_3, H_2O, N_2, CO, NO, O_2, CO_2, NO_2, and N_2O and a variety of organic ligands including saturated and unsaturated hydrocarbons. The kinetics of ligation has been followed as a function of the size and number of ligands and coordination numbers have been assigned accordingly. Here we report experimental investigations of the ligation kinetics of Fe^+, $(c\text{-}C_5H_5)Fe^+$, and $(c\text{-}C_5H_5)_2Fe^+$ with two cyanide molecules, HCN and HC_3N. These ligands were chosen for their high degree of unsaturation and their substantial polarizabilities and dipole moments. The reactions of these two cyanides with Fe^+ are also of interest in connection with the gas-phase ionic synthesis of metal cyanides, particularly as it may proceed in interstellar

environments. For example, for M = Mg, the following two-step interstellar synthesis has been proposed for MgCN [9]:

$$M^+HCN \rightarrow MNCH^+ \quad (2)$$

$$MNCH^+ + e \rightarrow MNC + H \quad (3)$$
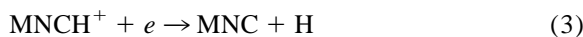
The metal isocyanide is produced in the second step by dissociative electron–ion recombination. Because of the extraordinarily low gas densities in interstellar environments, the first step in this synthesis must proceed by radiative association.

The gas-phase Fe^+, $(c\text{-}C_5H_5)Fe^+$, and $(c\text{-}C_5H_5)_2Fe^+$ chemistries of HCN and HC_3N appear not to have been investigated previously but reactions of saturated cyanides with Fe^+ have been studied in considerable detail using ion cyclotron resonance (ICR) [10] and Fourier transform-ICR (FT-ICR) [11] techniques. Investigations with these low-pressure techniques have shown that direct ligation with alkyl
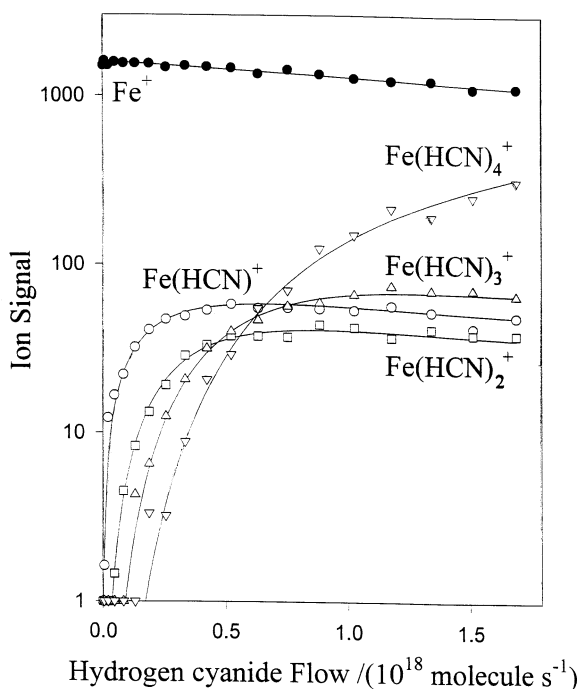
Fig, 1. Experimental data for the reaction of Fe^+ with HCN proceeding at 294 ± 3 K in helium buffer gas at a pressure of 0.35 ± 0.01 Torr. The lines represent fits of the experimental data for sequential pseudo-first-order kinetics.

cyanides is often pre-empted by intramolecular Fe^+ mediated cooperative effects of functional groups that lead to molecular elimination. However ligated ions sometimes do appear as products of secondary switching reactions. For example, the adduct Fe^+CNH was generated in this way and ligand-exchange bracketing measurements provided an estimate of the ligation energy, $34 < D(Fe^+ - NCH) < 37$ kcal mol^{-1} [12].

2. Experimental

The results reported here were obtained using a selected-ion flow tube (SIFT) apparatus which has been described previously [13,14]. All measurements were performed at a helium buffer-gas temperature of 294 ± 3 K and pressure of 0.35 ± 0.01 Torr. The reactant Fe^+ and $(c\text{-}C_5H_5)Fe^+$ ions were generated by electron impact at $20-60$ eV in a low-pressure (open)

ionization source directly from pure $(c\text{-}C_5H_5)_2Fe$ vapor. The ions were then mass selected, injected into the flow tube and allowed to thermalize by collisions ($\sim 4 \times 10^5$) with He buffer gas atoms before entering the reaction region downstream. The reactant neutrals were added as pure gases and the variation in reactant and product ion signals was monitored as a function of added reactant neutral. The hydrogen cyanide and cyanoacetylene were prepared with established laboratory procedures and used without further purification [15,16].

The data were analyzed in the usual fashion. Rate coefficients for primary reactions were obtained from a fit to the semilogarithmic decay of the primary ion with added neutral reactant. Higher-order rate coefficients were obtained by fitting the higher-order ion profiles to the solutions of the appropriate differential equations for sequential reactions. Also, in separate experiments, ligated ions were deliberately subjected to controlled multicollision induced dissociation (multi-CID) just prior to sampling by changing the potential of the sampling nose cone. The operation, advantages and limitations of this CID technique have been described in detail elsewhere [17].

3. Results and discussion

Table 1 summarizes the products and rate coefficients measured for the primary and higher-order ligation reactions initiated by Fe^+ and $(c\text{-}C_5H_5)Fe^+$ with HCN and HC_3N. Only ligation was observed; electron transfer is energetically unfavourable because of the high ionization energies of HCN and HC_3N, IE(HCN) = 13.6 eV and IE(HC_3N) = 11.6 eV [18], compared to IE(Fe) = 7.870 eV [19]. All rate coefficients are apparent bimolecular rate coefficients measured at 294 ± 3 K and a helium buffer-gas pressure of 0.35 ± 0.01 Torr and are compared with collision rate coefficients computed according to the algorithm of the combined variational transition-state theory developed by Su and Chesnavich [20] with $\alpha(\text{HCN}) = 2.59$ A$^{\circ 3}$ [21], $\mu_D(\text{HCN}) = 2.98$ Debye [22], $\alpha(HC_3N) = 5.29$ A$^{\circ 3}$ (calculated from bond and group polarizabilities) [23] and $\mu_D(HC_3N) = 3.72$ Debye [22].
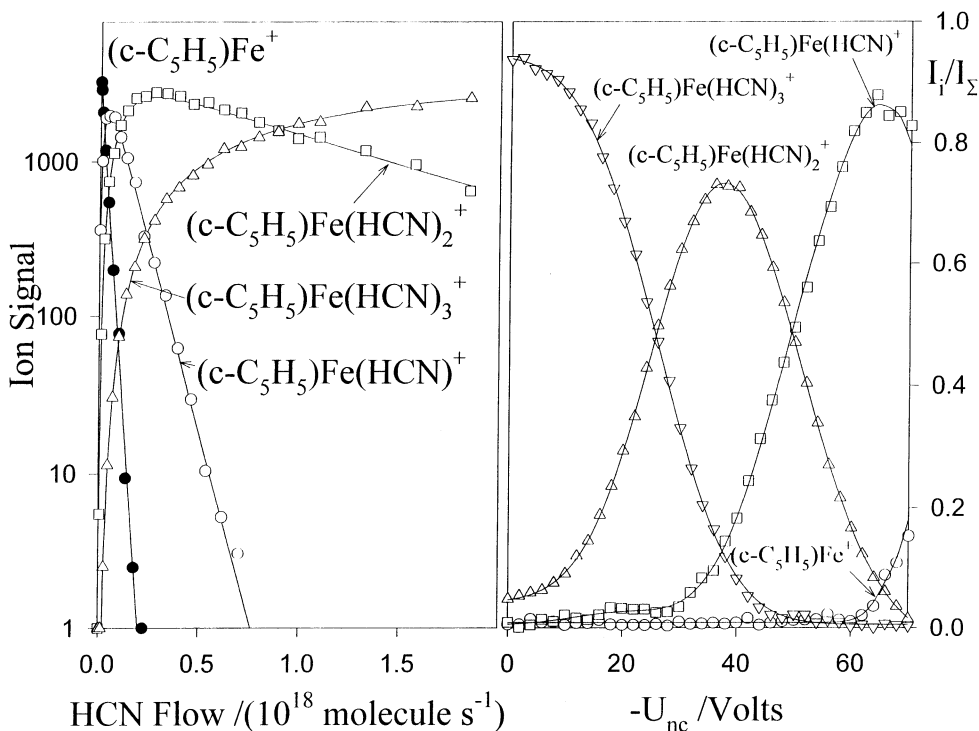
Fig, 2. (Left) Experimental data for the reaction of $(c\text{-}C_5H_5)Fe^+$ with HCN proceeding at 294 ± 3 K in helium buffer gas at a pressure of 0.35 ± 0.01 Torr. The lines represent fits of the experimental data for sequential pseudo-first-order kinetics. (Right) Multi-CID results for $(c\text{-}C_5H_5)Fe(HCN)_3^+$ in the laboratory energy scale and a flow of HCN = 2.5×10^{18} molecules s^{-1}.

The ligation is presumed to occur by termolecular association with the He buffer gas atoms acting as the stabilizing third body. However, radiative association, or a contribution by radiative association, could not be ruled out since the rate coefficients were not measured as a function of the total pressure of helium.

3.1. Reactions with HCN

HCN reacted slowly with Fe$^+$ under the chosen SIFT conditions with an apparent bimolecular rate coefficient, $k = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and an efficiency of only 4.5×10^{-3}. But, as can be seen in Fig. 1, the sequential additions of the next three molecules of HCN proceed rapidly with $k > 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} to ultimately produce Fe$^+$(HCN)$_4$. No Fe$^+$(HCN)$_5$ was observed to be

formed. $(c\text{-}C_5H_5)Fe^+$ reacted similarly but with some clear differences. Only three molecules of HCN added sequentially in total to ultimately produce $(c\text{-}C_5H_5)Fe^+(HCN)_3$ (see Fig. 2) and there were differences in the ligation kinetics. The initial ligation step is considerably faster with $(c\text{-}C_5H_5)Fe^+$, $k = 2.9 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, and proceeds essentially at every collision. Also, the rate of ligation declines noticeably with increasing number of ligands (see Table 1). The multi-CID spectrum shown in Fig. 2 clearly indicates sequential loss of the three HCN ligands in $(c\text{-}C_5H_5)Fe^+$ (HCN)$_3$. This result indicates that HCN ligates Fe$^+$ less strongly than does $(c\text{-}C_5H_5)$ and that no HCN interligand interaction is induced by $(c\text{-}C_5H_5)Fe^+$. $(c\text{-}C_5H_5)_2Fe^+$ did not react with HCN, $k < 1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. This observation implies that the ligand exchange reaction is endothermic or that $D(c\text{-}C_5H_5)Fe^+ - (c\text{-}C_5H_5) > D(c\text{-}C_5H_5)Fe^+ - (HCN)$.
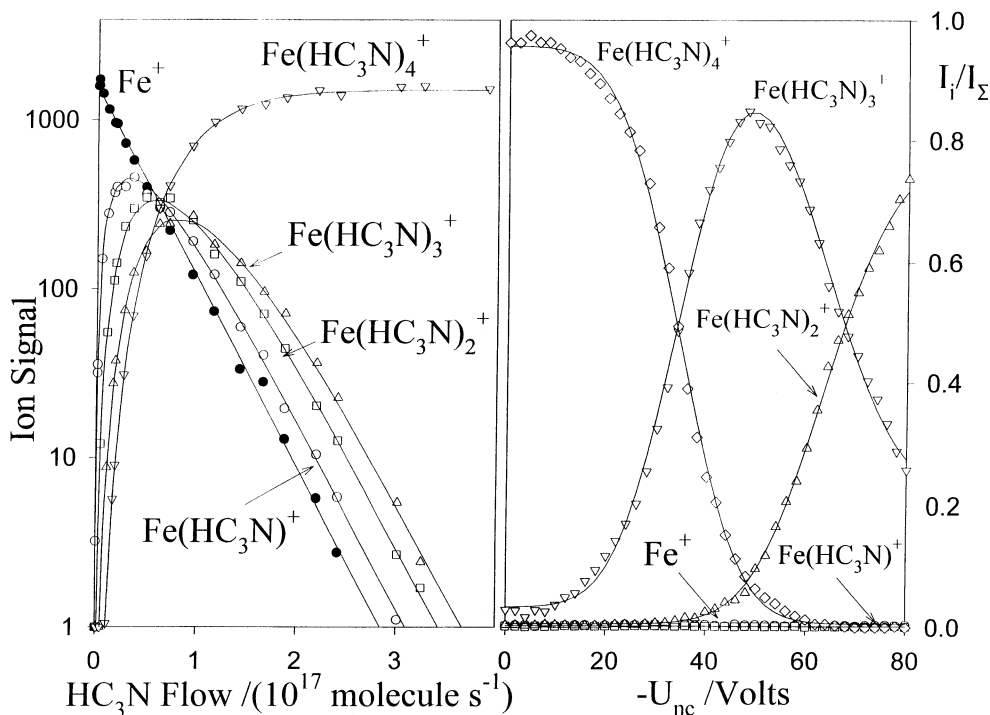
Fig. 3. (Left) Experimental data for the reaction of Fe^+ with HC_3N proceeding at 294 ± 3 K in helium buffer gas at a pressure of 0.35 ± 0.01 Torr. The lines represent fits of the experimental data for sequential pseudo-first-order kinetics. (Right) Multi-CID results for $Fe(HC_3N)_4^+$ in the laboratory energy scale and a flow of $HCN = 2.2 \times 10^{17}$ molecules s^{-1}.

3.2. Reactions with HC_3N

The first ligation reaction of HC_3N with Fe^+ is about 30 times faster than that of HCN under the chosen SIFT conditions, $k = 4.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Fig. 3 shows that further ligation remains rapid and that $Fe^+(HC_3N)_4$ is the ultimate product of the sequential ligation. Again the fifth adduct was not observed to be formed. The multi-CID spectrum shown in Fig. 3 indicates sequential loss of the four HC_3N ligands in $Fe^+(HC_3N)_4$ and this implies that no HC_3N interligand interaction is induced by Fe^+.

Fig. 4 shows that the sequential ligation of (c-C$_5$H$_5$)Fe$^+$ with HC_3N. The initial ligation step is fast, $k = 2.8 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, proceeding at essentially unit probability, and two more molecules of cyanoacetylene ligate sequentially ultimately to form (c-C$_5$H$_5$)Fe$^+$(HC$_3$N)$_3$. Further ligation is not observed. The multi-CID spectrum shown in Fig. 4

indicates sequential loss of the three HC_3N ligands in (c-C$_5$H$_5$)Fe$^+$(HC$_3$N)$_3$ and so suggests that HC_3N ligates Fe^+ less strongly than does (c-C$_5$H$_5$) and that no HC_3N interligand interaction is induced by (c-C$_5$H$_5$)Fe$^+$.

As with HCN, (c-C$_5$H$_5$)$_2$Fe$^+$ did not react with HC_3N, $k < 1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. So this observation implies that $D(c$-C$_5$H$_5$)Fe$^+ - (c$-C$_5$H$_5$) > D(c$-C$_5H_5$)Fe$^+ - (HC_3N)$.

3.3. Overview

Fig. 5 provides an overview of the variation in the apparent bimolecular rate coefficient for the sequential ligation of Fe^+ and (c-C$_5$H$_5$)Fe$^+$ by HCN and HC_3N with the number of ligands. These variations provide "titrations" of the effective cyanide coordination number for Fe^+ in the absence (clearly 4) and presence (clearly 3) of c-C$_5$H$_5$. Because of the high
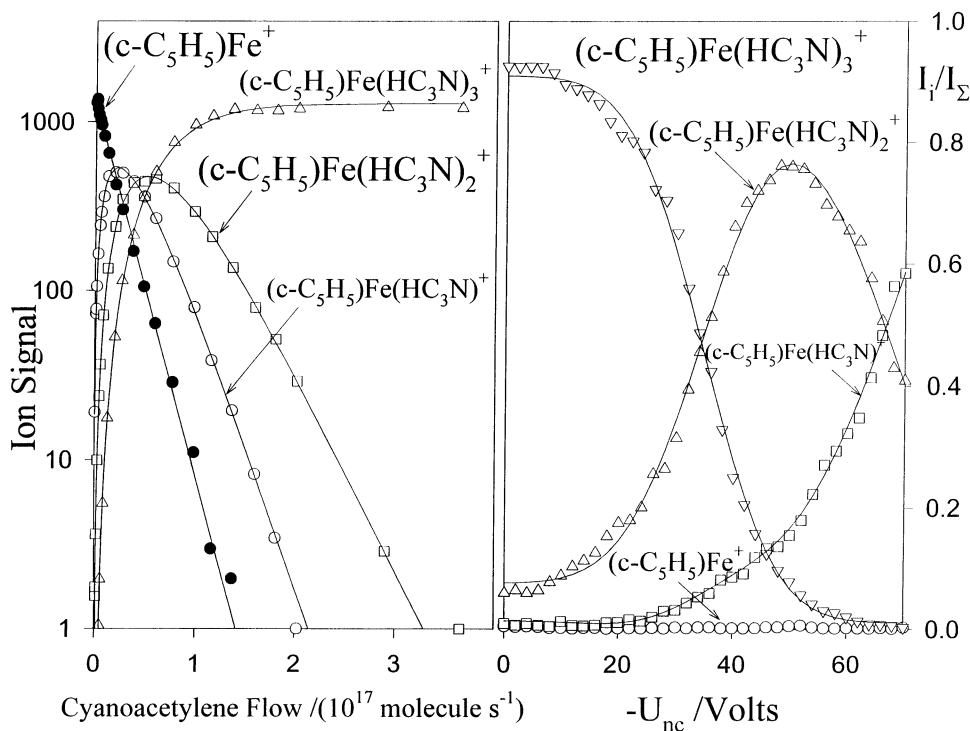
Fig. 4. (Left) Experimental data for the reaction of $(c\text{-}C_5H_5)Fe^+$ with HC_3N proceeding at 294 ± 3 K in helium buffer gas at a pressure of 0.35 ± 0.01 Torr. The lines represent fits of the experimental data for sequential pseudo-first-order kinetics. (Right) Multi-CID results for $(c\text{-}C_5H_5)Fe(HC_3N)_3^+$ in the laboratory energy scale and a flow of $HCN = 1.6 \times 10^{17}$ molecules s^{-1}.

dipole moments of these two cyanides with the negative end at the nitrogen, coordination can be expected to proceed end-on to produce the isocyanide as in $M^+ - NCH$ in which :NCH acts as a $2e$ donor.

A number of differences are observed in the variations in rate coefficient for ligation. We attribute the more than two order-of-magnitude increase in the initial rate of ligation of Fe^+ with HC_3N over that with HCN to the degree-of-freedom effect associated with termolecular addition reactions as a consequence of the formation of a transient intermediate. The lifetime of the intermediate against back dissociation that depends both on the degrees of freedom effective in intramolecular energy redisposition in the intermediate $(ML_{n+1}^+)^*$ and on its attractive well depth, $D(ML_n^+ - L)$, viz. the ligation energy of ML_n^+. The reactivity of the Fe^+ ^6D $(4s^1 3d^6)$ ground state also is expected to be hindered somewhat by the necessity to promote the electron from the large outer shell s orbital to the more compact

higher-energy d orbital and this may contribute to the depressed rate constant for the addition of the first ligand to Fe^+. The $4s$ to $3d$ electron promotion would leave the $4s$ and $4p$ orbitals available for ligation and so account for the observed addition of a maximum of four $2e$ donor cyanide ligands.

The higher initial rates of ligation of $(c\text{-}C_5H_5)Fe^+$ with HCN and HC_3N compared to Fe^+ can be attributed entirely to the degrees-of-freedom effect. The drop in the rate of ligation of $(c\text{-}C_5H_5)Fe^+$ with increasing n seen for the ligation of $(c\text{-}C_5H_5)Fe^+$ with HCN, and less so with HC_3N, can be attributed to a possible drop in the ligation energy with n. The apparent higher ligation energy of HC_3N is consistent with its significantly higher polarizability and dipole moment.

The bonding in the $^5E_2$ ground-electronic state of $(c\text{-}C_5H_5)Fe^+$ can be understood in terms of electron transfer from Fe^+ to the $c\text{-}C_5H_5$ ligand to form $(c\text{-}C_5H_5)^- Fe^{2+}$ and back donation from the six π
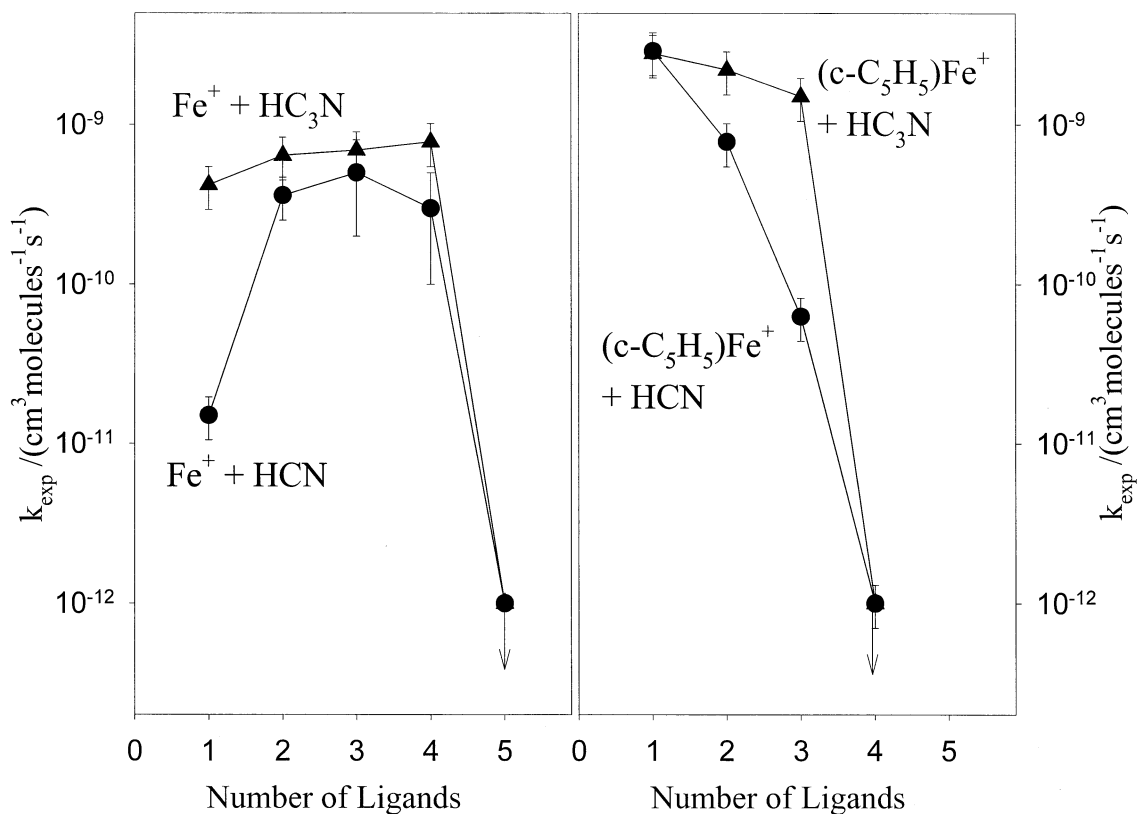
Fig. 5. (Left) Variation in the apparent bimolecular rate coefficient for the sequential ligation of Fe^+ by HCN and HC_3N with the number of ligands in helium bath gas at 294 ± 3 K and a pressure of 0.35 ± 0.01 Torr. The increasing uncertainty in k is associated with the propagation of uncertainty in the profile fitting procedure. (Right) Variation in the apparent bimolecular rate coefficient for the sequential ligation of $(c\text{-}C_5H_5)Fe^+$ by HCN and HC_3N under similar conditions.

electrons in $(c\text{-}C_5H_5)^-$ to primary $4s$ and $4p$ orbitals of Fe^{2+}. Such bonding leaves one orbital available for the initial ligation and further ligation requires a change in multiplicity. The ligated $(c\text{-}C_5H_5)Fe^+$ $(RCN)_3$ species have 18-electron shells around the iron and so are coordinatively saturated.

Possible structures assuming sp^3 hybridization for the HC_3N ligated species $Fe^+(HC_3N)_4$ and $(c\text{-}C_5H_5)Fe^+(HC_3N)_3$ are shown in Fig. 6.

4. Conclusions

We have shown that gas-phase rate coefficient measurements for the sequential ligation of bare and ligated Fe^+ ions with strongly polar ligands proceeding in an inert bath gas at moderate pressures can provide a useful means to titrate for intrinsic Fe coordination numbers. HCN and HC_3N appear to behave as classic $2e$ donor ligands. The observation of collisional association of the two cyanides with Fe^+ argues in favour of the possible formation of the isocyanide molecules FeNC and $FeNC_3$ in interstellar environments in a reaction sequence involving radiative association followed by dissociative recombination with electrons, reactions (2) and (3).
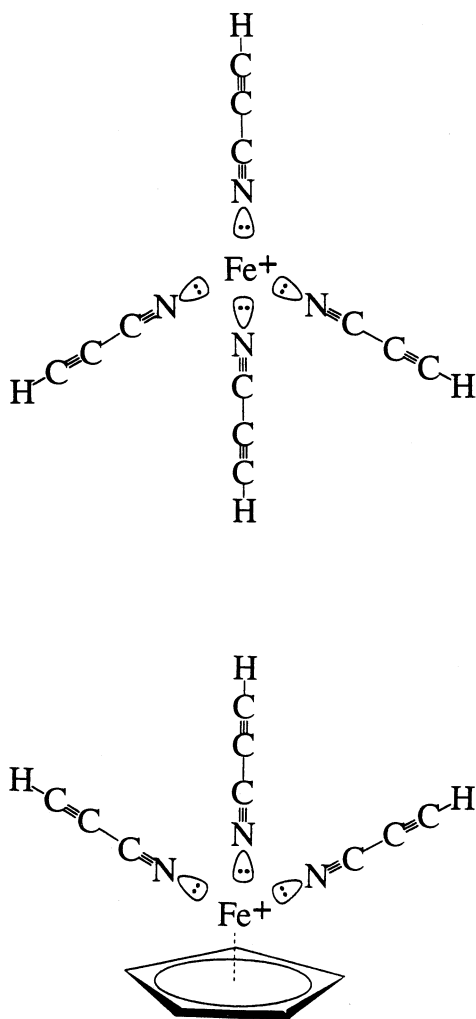
Fig. 6. Possible structures for Fe(HC₃N)₄⁺ and (c-C₅H₅)Fe(HC₃N)₃⁺.

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