Ligand Effects on the Gas-Phase Reactions of $(\pi\text{-L})Fe^I$ Complexes with *n*-Pentanenitrile

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The gas-phase ion chemistry of the previously studied system Fe(*n*-pentanenitrile)$^+$ is dramatically changed, when the metal ion bears substituents L (L = C_2H_4, C_3H_6, C_4H_6, *i*-C_4H_8, 1-C_4H_8, 2-C_4H_8, and C_6H_6), and the major ion-molecule reactions of Fe(L)$^+$ with RCN (R = *n*-C_4H_9) are as follows: (i) Ligand substitution Fe(L)$^+$ + RCN → Fe(RCN)$^+$ + L is observed for all L studied except L = C_4H_6, C_6H_6; (ii) the formation of association complexes Fe(L)(RCN)$^+$ takes place for all ligands L, except L = C_2H_4; (iii) dehydrogenation of the L is confined to L = 1-C_4H_8 and 2-C_4H_8; (iv) carbon–carbon and carbon–nitrogen bond activation of the nitrile, typical for the behaviour of *bare* Fe$^+$, are absent in the reactions of all Fe(L)$^+$ with RCN. Dehydrogenation of the nitrile is observed only for

L = 1-C_4H_8 and 2-C_4H_8, and the molecular hydrogen originates exclusively from the γ/δ-position of the alkyl chain following the well-established "remote functionalization" concept. In contrast to the reaction of *bare* Fe$^+$ with *n*-pentanenitrile, dehydrogenation in the Fe(L)(RCN)$^+$ system is *not* preceded by a degenerate isomerization of RCN, bringing about equilibrations of the C(α)/C(γ) positions. Rate constants were derived and compared with those calculated by the ADO and CAP theories. All reactions of the ligated Fe(L)$^+$ ions were found to occur with collision rate, again in contrast to the bare Fe$^+$. Based on the ADO formalism, the dipole locking constant "*c*" of *n*-pentanenitrile was redetermined to *c* = 0.47.

The gas-phase reaction of *bare* Fe$^+$ with RCN (R = *n*-C_4H_9) differs from that of long-chain alkanenitriles and many other monofunctional alkanes in that the straightforward mechanism of *remote functionalization*[1] is in competition with some intriguing processes[2]: While loss of molecular hydrogen (73%) is due to remote functionalization (C–H bond activation of the $\omega/\omega - 1$ positions of the alkyl chain), ethylene is produced (23%) from *internal* positions, generating CH_3–Fe$^+$–CH_2CN as product. Loss of propene is also observed in low abundance (1%), producing an Fe$^+$(CH_3CN) complex. All three processes are in competition with the unprecedented formation of the ferracyclobutane complex I (Scheme 1), which, upon reopening, brings about equilibration of the α- and γ-positions, thus affording a specific, degenerate isomerization of the Fe(RCN)$^+$ collision complex.
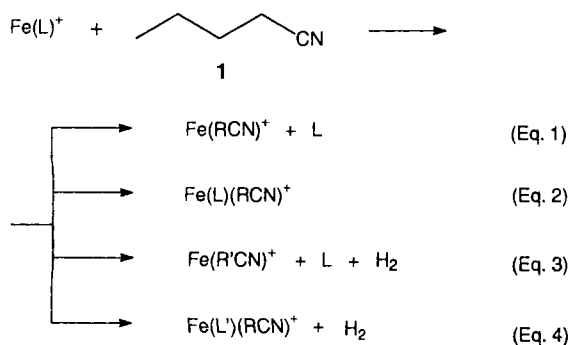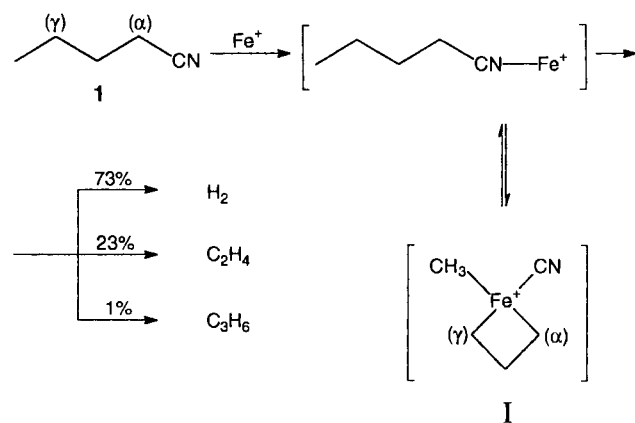
In view of the fact, that the intrinsic properties of the transition-metal ions M$^+$ in their gas-phase reactions with organic substrates are affected by ligands L[1b,3], and because of the unique behaviour of the Fe$^+$/*n*-pentanenitrile system, we have dediced to study the effects of some representative π-ligands L (L = C_2H_4, C_3H_6, C_4H_6, *i*-C_4H_8, 1-C_4H_8, 2-C_4H_8, and C_6H_6) in the ion-molecule reactions of Fe(L)$^+$ and RCN by using Fourier transform ion cyclotron resonance mass spectrometry. The quite surprising results are reported in this article, and in addition we will also compare the experimentally determined rate constants with those predicted by the ADO and CAP formalisms.

Results and Discussion

The reaction products and branching ratios of the Fe(L)$^+$/RCN systems are given in Scheme 2 and Table 1. Although the actual structures of the product ions are unknown, the investigation of deuterium-labeled isotopomers of RCN together with low-energy collision experiments provide some mechanistic insight as well as information on the gross-structural features of the product ions.

The importance of the latter aspect is highlighted by recalling that M[R′,N,C,O]$^+$ complexes (R′ = branched alkyl) do not necessarily correspond to a simple M(R′NCO)$^+$ adduct; rather, in the course of the ion-molecule reactions quite unexpected isomerizations took place which resulted in the formation of M(alkene)(HNCO)$^+$ clusters[4]. Obviously, attachment of the ligand R′NCO to the metal ion is followed by C–N and C–H bond activation. In order to clarify this

Scheme 1

Fe(L)$^+$ +   [structure: pentanenitrile chain] CN   →

1

$$Fe(RCN)^+ + L \qquad (Eq. 1)$$

$$Fe(L)(RCN)^+ \qquad (Eq. 2)$$

$$Fe(R'CN)^+ + L + H_2 \qquad (Eq. 3)$$

$$Fe(L')(RCN)^+ + H_2 \qquad (Eq. 4)$$

Scheme 2

Table 1. Branching ratios for the reactions of the Fe(L)$^+$ complexes with n-pentanenitrile according to Scheme 2

Fe(L)$^+$	Eq. (1)	Eq. (2)	Eq. (3)	Eq. (4)	BDE(Fe$^+$–L) [kcal/mol][7,8]
Fe(C$_2$H$_4$)$^+$	1.00	–	–	–	34
Fe(C$_3$H$_6$)$^+$	0.79	0.21	–	–	37
Fe(1-C$_4$H$_8$)$^+$	0.13	0.10	0.04	0.73	40
Fe(2-C$_4$H$_8$)$^+$	0.13	0.10	0.04	0.73	40
Fe(i-C$_4$H$_8$)$^+$	0.51	0.46	0.03	–	40
Fe(C$_4$H$_6$)$^+$	–	1.00	–	–	48
Fe(C$_6$H$_6$)$^+$	–	1.00	–	–	55

aspect for the Fe(L)$^+$/RCN systems, all product ions mentioned in Scheme 2 were subjected to low-energy collision-induced dissociation (CID) experiments ($E_{lab} = 1 - 40$ eV), and these results are presented first.

For the product Fe(RCN)$^+$ formed in Eq. (1) it was found that, irrespective of the ligand L, in a CID experiment the entire RCN group was eliminated. This indicates the absence of an isomerization reaction of n-pentanenitrile analogous to that of R'NCO.

For the association products (Eq. 2), depending on the collision energies, we observe evaporation of L, RCN or of both ligands. No other neutrals are generated upon collisional activation. Interestingly, for the complexes Fe(L)-(RCN)$^+$ with L = i-C$_4$H$_8$, 1-C$_4$H$_8$, 2-C$_4$H$_8$ or C$_4$H$_6$, we do *not* observe upon CID products which might point to the operation of an *interligand* double-hydrogen atom transfer. This gas-phase analogue of the Crabtree-Felkin process[5], for which two examples have been reported recently[6], is not operative in the present systems.

CID of the Fe(R'CN)$^+$ complexes (Eq. 3), formed in the reaction of Fe(C$_4$H$_8$)$^+$ with RCN by loss of molecular hydrogen or double-hydrogen transfer to C$_4$H$_8$, liberates R'CN at all kinetic energies; this points to the presence of an intact dehydrogenated nitrile (for details see further below). The connectivity of the cluster Fe(L')(RCN)$^+$, formed in Eq. (4) for ligands L = 1-C$_4$H$_8$, 2-C$_4$H$_8$, can also be deduced from a CID experiment. For collision energies $E_{lab} \leqslant 8$ eV, expulsion of intact RCN is observed; at higher energies loss of C$_4$H$_6$ (presumably 1,3-butadiene) occurs in competition with RCN evaporation.

In conclusion, irrespective of the nature of the ligand L, in the ion-molecule reactions of Fe(L)$^+$ with RCN, there is no indication whatsoever for a C–C or a C–N bond activation of the n-pentanenitrile. This finding already points to the existence of a pronounced ligand effect, when compared with the reactivity of *bare* Fe$^+$ with CH$_3$[CH$_2$]$_3$CN.

Next we will discuss in more detail the reactions described in Scheme 2 and Table 1.

As the bond dissociation energy (BDE) of Fe$^+$ –(RCN) is ca. 42 kcal/mol[7], ligand exchange according to Eq. (1) is expected to occur for L = C$_2$H$_4$, C$_3$H$_6$, i-C$_4$H$_8$, 1-C$_4$H$_8$, and 2-C$_4$H$_8$ [BDE(Fe$^+$–L) < 42 kcal/mol[8]], but not for C$_4$H$_6$ and C$_6$H$_6$ [BDE(Fe$^+$–L) > 48 kcal/mol[8]]. This is indeed observed experimentally (Table 1).

Ligand association (Eq. 2) is found to occur for L = C$_4$H$_6$ and C$_6$H$_6$ as the only reaction. While infrared-radiative cooling[9] may account for this behaviour, we believe that the absence of the processes described in Eq. (1), (3), and (4) for these Fe(L)$^+$ systems can be explained in more simple terms: As already mentioned, ligand substitution (Eq. 1) is not possible on energetic grounds [BDE(Fe$^+$–L) > BDE(Fe$^+$ – (RCN))]. This energetic aspect also holds true for the dehydrogenation of RCN, associated with ligand replacement (Eq. 3), as well as dehydrogenation of butadiene (to generate C$_4$H$_4$) and benzene (to produce C$_6$H$_4$) (Eq. 4). The consideration of available thermochemical data[7,8] clearly demonstrates that the reactions described in Eq. (3) and (4) are very endothermic for L = C$_4$H$_6$ and C$_6$H$_6$.

As already mentioned, C–C and C–N bond activation of the nitrile is absent for reactions with *all* Fe(L)$^+$ complexes. Similarly, C–H bond activation (Eq. 2) is also a minor process, and is observed only for the three isomeric Fe(C$_4$H$_8$)$^+$ systems with branching ratios of 3 and 4%, respectively (Table 1). For all other ligands studied, this reaction does not take place. Obviously, ligation of the metal ion has a profound effect on its reactivity with the nitrile. With regard to the dehydrogenation of n-pentanenitrile by Fe(C$_4$H$_8$)$^+$ it is, of course, interesting to know as to whether this reaction has anything in common with the unusual behaviour of the more simple Fe$^+$/RCN system (Scheme 1). To this end, we have allowed all three Fe(C$_4$H$_8$)$^+$ complexes to react with specifically labelled isotopomers of RCN, i.e. CD$_3$[CH$_2$]$_3$CN (**1a**), CH$_3$CD$_2$[CH$_2$]$_2$CN (**1b**), CH$_3$CH$_2$CD$_2$CH$_2$CN (**1c**), and CH$_3$[CH$_2$]$_2$CD$_2$CN (**1d**). The result is unambiguous in that molecular hydrogen originates exclusively from the γ/δ-positions, and the reaction follows the familiar "remote functionalization" pattern of a 1,2-elimination introducing a terminal double bond. This reaction is absolutely clean in that it is neither preceded by hydrogen scrambling nor by an equilibration reaction of the α/γ-position, which has been observed for *bare* Fe$^+$ [2]. We conclude, that ligation of Fe$^+$ does not only suppress C–C and C–N bond activation processes of n-pentanenitrile (**1**), it also brings about a simplification of the dehydrogenation path in that a metallacyclic intermediate, analogous to **I**, is not involved.

The next question to be addressed in this context concerns the "nature" of molecular hydrogen liberated by the dehydrogenation of n-pentanenitrile: Is H$_2$ eliminated as a gen-

uine species together with the ligand L — as indicated in Eq. (3) — or does the metal ion mediate *interligand* double-hydrogen atom transfer from the RCN group to C_4H_8 with the consequence that C_4H_{10} rather than C_4H_8/H_2 is formed[10]? As the exact nature of the neutrals generated in ion-molecule reactions cannot be inferred by using our set-up, one has to rely on more indirect criteria. For example, thermochemical considerations are helpful to rule out a reaction path if this is predicted to be *endo*thermic for a particular product combination. For the reactions in question, i.e. the formation of H_2 *and* C_4H_8 in Eq. (3) we estimate[11] a heat of reaction of $\Delta H_r = -5$ kcal/mol while for the production of genuine C_4H_{10} ΔH_r is calculated to -32 kcal/mol. Thus, on thermochemical grounds, in principal *both* reactions are possible, and further experiments are indicated to settle this problem.

Next, we will mention briefly that dehydrogenation of the *ligand* L in the reaction with RCN (Eq. 4) is confined to L = 1-C_4H_8 and 2-C_4H_8, and the large branching ratio of 73% is clearly caused by the formation of a particularly stable Fe(1,3-butadiene)(RCN)$^+$ complex. The absence of ligand C–H bond activation in all other Fe(L)$^+$ systems is not surprising as dehydrogenation according to Eq. (4) is very endothermic. For the Fe(C_6H_6)(RCN)$^+$ complex formed via Eq. (4) we estimate an upper limit for the complex' heat of formation of $\Delta H_f < 217$ kcal/mol.

In the following, we will discuss the experimentally determined rate constants, k_R, for the reactions of RCN (R = C_4H_9) with Fe(L)$^+$ and compare this with calculated rate constants as predicted by various theoretical approaches. For the sake of completeness we also include in Table 2 the experimental and theoretical rate constants for the reaction of *bare* Fe$^+$ with $CH_3[CH_2]_3CN$. The complexes Fe(L)$^+$ are listed in the order of increasing bond

dissociation energies. It should be mentioned that in a semi-log plot the temporal disappearance of the Fe(L)$^+$ signal intensity was linear; this indicates the absence of kinetically or electronically excited Fe(L)$^+$ species.

In comparison to the Fe(L)$^+$ complexes, the reaction of the *bare* metal ion is by a factor of ca. 3 *slower*. When compared with the various theoretically derived rate constants, the Langevin theory seems to match the experimental results best for the reaction of Fe$^+$, but is by a factor of ca. 3 too slow for describing the reaction rates of Fe(L)$^+$. However, as the Langevin theory does not take into account ion-dipole attractions, the predicted values are generally expected too small; and consequently, the agreement with k_R for the reactions of Fe$^+$ may be fortuitous.

By using the ADO approach[13,17], one obtains rate constants which, for the Fe(L)$^+$ sytem, are too small by a factor of ca. 1.5, while assuming complete locking of the dipole ($\rightarrow$ k_{CLD}) results in overestimation of the number of effective collisions for these systems; consequently, the calculated k_{CLD} are too high by a factor of ca. 2. The best agreement between theory and experiment is found for k_{CAP}. The slight deviation is due to (i) the error bars of the experiments and (ii) the assumption of point-charges and of potentials only due to ion-induced dipole and ion-permanent dipole interactions in the CAP theory[16]. We conclude that the reactions of Fe(L)$^+$ with n-C_4H_9CN occur at collision rate. In contrast, for the *bare* metal ion only one in three collisions gives rise to products. We believe that the decreased reactivity of Fe$^+$ directly reflects the fact that *bare* Fe$^+$ in its reaction with n-C_4H_9CN *invariably involves tight transition structures* (see Scheme 1 and the more detailed analysis of data given in ref.[2]), thus imposing barriers on the reaction coordinates. In contrast, the ligated systems Fe(L)$^+$ — except for the quite minor reaction channel (ca. 3%) of dehydrogenation of the nitrile (Eq. 3) — enjoys a much less confined scenario in that most of the reactions with n-C_4H_9CN are simple ligand substitutions, association reactions or a sterically much less demanding dehydrogenation of the n-butene ligands.

Finally, the set of data reported in Table 2 allows a redetermination of the dipole locking constant c which — for nitriles — has caused in the past some difficulties in successfully applying the ADO approach[13,17]; c is defined in ref.[17], and from the assumption[13] that the so-corrected rate constant k_{ADO} equals k_R an expression for c derives (Eq. 6). The so-obtained dipole locking constant c (Table 2) gives a mean value of $c = 0.47$ for n-pentanenitrile which contrasts with the previously used number of $c = 0.255$[13].

Table 2. Experimentally determined rate constants k_R for the reactions of Fe$^+$ and Fe(L)$^+$ with n-C_4H_9CN and calculated rate constants as predicted by Langevin, ADO, CLD, and CAP theories[a]

Ion	k_R	k_L	k_{ADO}[b]	k_{CLD}[c]	k_{CAP}[d]	k_R/k_{CAP}	c
Fe$^+$	12	12.8	28.7	79.2	36.0	0.33	—
Fe(C_2H_4)$^+$	35	11.4	25.7	70.9	32.2	1.09	0.40
Fe(C_3H_6)$^+$	38	11.0	24.7	68.3	31.0	1.23	0.47
Fe(1-C_4H_8)$^+$	37	10.7	24.0	66.3	30.1	1.23	0.47
Fe(2-C_4H_8)$^+$	38	10.7	24.0	66.3	30.1	1.27	0.49
Fe(i-C_4H_8)$^+$	38	10.7	24.0	66.3	30.1	1.27	0.49
Fe(C_4H_6)$^+$	37	10.7	24.1	66.6	30.3	1.22	0.46
Fe(C_6H_6)$^+$	37	10.3	23.2	64.0	29.1	1.27	0.50

[a] The estimated error of k_R is $\pm 25\%$ [7]; the error is mostly due to different ion gauge sensitivities for different substances in comparison with rate constants taken as references from the literature[12]; all rate constants are given in units of 10^{-10} cm^3/(s · molecule). — [b] k_{ADO} (*A*veraged *D*ipole *O*rientation) calculated according to the revised method of Su et al.[13,17]. — [c] k_{CLD} (*C*ompletely *L*ocked-in *D*ipole) is calculated based on k_{ADO}; the dipole locking constant c (as defined in Eq. (5) and (6) in the text and in ref.[17]) depends on the polarizability α and the dipole moment μ_D; α(RCN) was calculated by using the Miller-Savchik formula[14] yielding $\alpha = 9.95$ Å^3; the dipole moment of n-C_4H_9CN ($\mu_D = 4.12$ D) was taken from the literature[15]. — [d] k_{CAP} (*c*apture rate constant) was calculated as described in ref.[16].

$$k_{ADO} = k_L + c(k_{CLD} - k_L) \qquad \text{(Eq. 5)}$$

$$\text{with } k_{ADO} = k_R$$

$$c = (k_R - k_L)/(k_{CLD} - k_L) \qquad \text{(Eq. 6)}$$

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Experimental

The labeled *n*-pentanenitriles **1a—d** were synthesized according to established techniques, purified by preparative gas chromatography, and characterized by NMR spectroscopy and GC/MS. The ion-molecule reactions were studied by using the technique of Fourier transform ion cyclotron resonance (FTICR)[18] mass spectrometry, and the experiments were performed by using a Spectrospin CMS 47X Fourier transform ion cyclotron resonance mass spectrometer which is equipped with an external ion source[19]; the instrument and further details of its operation have been previously described[20]. Briefly, Fe^+ ions were generated by laser desorption/ionization[21] by focussing the beam of a Nd:YAG laser (Spectron Systems: $\lambda = 1064$ nm) onto a stainless-steal target, which is affixed in the external ion source. The ions are extracted from the source and transferred into the analyser cell by a system of electrostatic potentials and lenses. The ion source, transfer system, and ICR cell are differentially pumped by three turbo-molecular pumps (Balzers TPU 330 for source and cell and Balzers TPU 50 in the middle of the transfer system). After deceleration, the ions are trapped in the field of the superconducting magnet (Oxford Instruments), which has a maximum field strength of 7.0 T. The metal's most abundant isotope is isolated by using FERETS[22]. For collisional cooling of any excited states possibly formed and removal of kinetic energy remaining from the transfer, argon was present as a buffer gas with a constant "background" pressure of ca. 5×10^{-7} mbar, as measured with an ionization gauge (Balzers IMG 070). For CID experiments[23] argon was also employed. For the generation of the $Fe(L)^+$ complexes the reagent gases were introduced through pulsed valves[24], and literature-known procedures were employed[25]. The complexes were isolated by double-resonance ejection, and great care was applied to avoid any off-resonance excitation of the ion of interest while ejecting the ^{13}C isotope signals[26]. For the reaction of $Fe(L)^+$ with *n*-pentanenitrile (and its isotopomers), the nitriles were admitted to the ICR cell by a leak valve ($p_{cell} \approx 6 \times 10^{-9}$ mbar). The elementary compositions of the ions were determined by applying high-resolution FTICR as described earlier[20a,c].

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[10] The latter possibility, i.e. the Fe^+-mediated *interligand* hydrogen-atom transfer has been recently uncovered for the oxidation of ethanol and 2-propanol by $Fe(C_4H_6)^+$ (see ref.[3b]); see also ref.[3a], in which the dehydrogenation of 4-heptanone by $Fe(C_4H_6)^+$ is discussed as an example for an *interligand* double-hydrogen atom transfer.

[11] Heats of reaction were estimated by using the known[7,8] heats of formation of $Fe(C_4H_8)^+$, $CH_3[CH_2]_3CN$, and C_4H_{10}. $\Delta H_f[Fe(R'CN)]$, i.e. the Fe^+ complex of pent-4-enenitrile, was estimated to $\Delta H_f = 262$ kcal/mol, by using ΔH_f(pent-4-enenitrile) = 30 kcal/mol and BDE[$Fe^+ - (R'CN)$] = 49 ± 7 kcal/mol; this BDE was obtained from two ligand exchange reactions of Fe^+ complexes: From the observation that R'CN is replaced by benzene but not by RCN, the bond dissociation energy of $Fe^+ - (R'CN)$ can be bracketed to 42 < BDE[$Fe^+ - (R'CN)$] < 55 kcal/mol. — We note in passing that a BDE of 49 ± 7 kcal/mol strongly suggests a *bidentate* bonding of the terminal double bond *and* the CN multiple bond (the latter presumably acting in a *side-on* fashion of the pentenenitrile to the metal ion); for further examples of a bidentate bonding of two functional groups to Fe^+, see: [11a] T. Prüsse, T. Drewello, C. B. Lebrilla, H. Schwarz, *J. Am. Chem. Soc.* **1989**, *111*, 2857. — [11b] T. Prüsse, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1991**, *110*, 237.

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