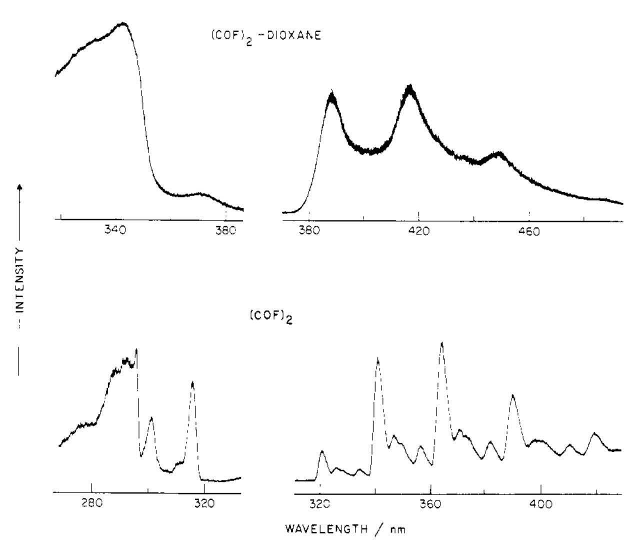

Figure 3. Phosphorescence emission and uncorrected photoexcitation spectra at 4.2 K of neat oxalyl fluoride and its complex with 1,4-dioxane.

in good agreement with the mean O(dioxane)···C distance of 2.60 Å found in the dioxane complex. At the optimized geometries, the energy of the model complex was lower than the sum of the energies of its moieties by 7–30 kcal/mol, depending on the basis set, which exceeds the expected difference in the zero-point energies. The geometries of the water and oxalyl fluoride at the optimized geometry for the model complex remained essentially unchanged from those of the free molecules. The agreement between the calculated and experimental geometries for oxalyl fluoride is poor for the data obtained from the dioxane complex but reasonable for the gas-phase data, which again suggest some disorder in the crystals of the complex.

The interaction between the waters and the oxalyl fluoride can be loosely described as "charge-transfer" bonding, wherein each water donates charge to the oxalyl fluoride (an average of 0.025 e for the three basis sets). The largest change that results within the oxalyl fluoride is a redistribution of the $2p\pi$ orbital populations. The gross $2p\pi$ orbital populations of the carbons decrease while those of the oxygens, and to a lesser extent the fluorines, increase relative to uncomplexed oxalyl fluoride. Concomitantly, the Mulliken overlap population for the π orbitals of the carbons is reduced in the complex (0.0097 vs. 0.0087 in STO-3G). The largest overlap population between the waters and the oxalyl fluoride involves the $2p\pi$ orbitals of the carbons and the parallel $2p_z$ orbitals on the oxygens of the waters (0.0007 in STO-3G).

Calculations were not done for any excited states. However, the changes in the HOMO and LUMO energies suggest that the ${}^{1,3}A_u$–${}^{1}A_g$ transitions of oxalyl fluoride would blue shift upon complexation, contrary to the observed results. Presumably, the excited states are somehow stabilized by the interactions, or the observed spectra are not due to bulk oxalyl fluoride in the crystal.

Acknowledgment. We thank Professor W. H. Fink for making available the GAUSSIAN 82 programs and Z. Darakjian for aid in their use.

The Reaction of Nitriles and Fe^+ in the Gas Phase. A Case of Remote Functionalization

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Abstract: The gas-phase reaction of bare Fe^+ atoms with linear alkyl nitriles generates "end-on" complexes (**1**) which, depending on geometrical constraints, specifically interact with remote C–H bonds. Based on chain length effect studies and the investigation of labeled precursors, a mechanism is suggested which accounts for the chemospecificity observed for the loss of H_2 and C_2H_4 from RCN/Fe^+ complexes. This mechanism does not follow the analogous reaction of Fe^+ with alkenes and alkynes but involves an initial C–H insertion of the remote CH bonds followed by a C–C insertion.

The selective functionalization of C–H bonds remains one of the major focuses of catalytic and organic chemistry. In solution chemistry, high selectivity is often obtained by the presence of activating groups which induce the reactivity of the neighboring C–H bonds by, for example, polarizing the bond, thus making the hydrogen more acidic, or by generally weakening the C–H bond.[1] In the reactions of metals, both in the gas phase and in the bulk phase, activation of the neighboring C–H groups is accomplished selectively by initial complexation of the functional group and the metal.[2,3,4] Hence, allylic activation has widely been observed both in heterogeneous catalysis and in the gas phase with a variety of metals. Conversely, the functionalization of *remote* C–H bonds, i.e., several carbon atoms away from the functional group, remains a challenge. Such reactions are nonetheless

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(1) Several basic organic chemistry books exist on the functionalization of activated C–H bonds. Some examples: (a) March, J. *Advanced Organic Chemistry-Reactions, Mechanisms, and Structure*; Wiley: New York, 1985. (b) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1981.

(2) (a) Lebrilla, C. B.; Maier, W. F *J. Am. Chem. Soc.* **1986**, *108*, 1606. (b) Rooney, J. J. *J. Catal.* **1983**, *2*, 53. (c) Burwell, R. L., Jr.; Shim, B. C. C.; Rowlinson, H. C. *J. Am. Chem. Soc.* **1953**, *79*, 5142.

(3) (a) Larsen, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912. (b) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998. (c) Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2543. (d) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484. (e) Tsarbopoulos, A.; Allison, J. *J. Am. Chem. Soc.* **1985**, *107*, 5085. (f) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (g) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360.

(4) (a) Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Chem. Soc.* **1984**, *106*, 4307. (b) Schulze, C.; Steinrück, N.; Weiske, T.; Schwarz, H.; Gross, M. L., unpublished results. (c) Peake, D. A.; Gross, M. L. *Organometallics* **1986**, *5*, 1236.

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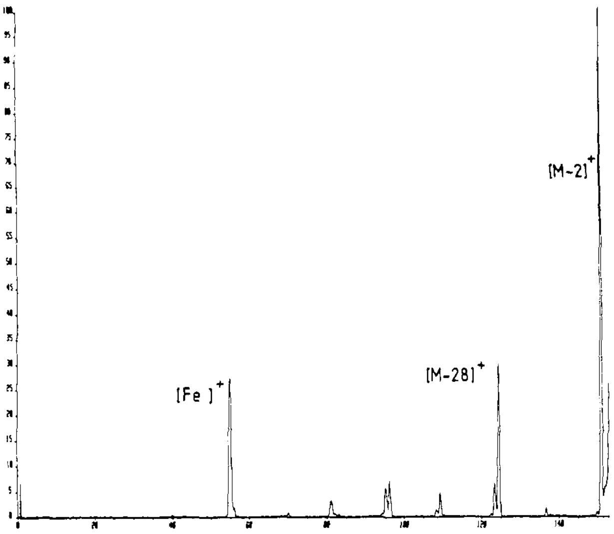

Figure 1. CA spectrum of $CH_3(CH_2)_4CN/Fe^+$.

common among enzymes which coordinate the functional group and geometrically select a specific site on the substrate.[5] The term "remote functionalization" has been coined by Breslow.[5a,b] This method of coordination and selective reactions has been principally illustrated by Breslow et al. on a variety of systems, an example of which is the epoxidation of remote double bonds in steroids.[5d] Our preliminary studies show that a similar system exists also in the gas phase, specifically for the reaction of linear nitriles and Fe^+. Due to the specific binding of Fe^+ to the CN group, C–H bonds near the CN group are geometrically unavailable for insertion by Fe^+, while those at least five carbons away are readily activated.[6]

Experimental Section

Fe^+ is generated from $Fe(CO)_5$ by electron impact (70 eV). A ZAB-HF-3HF triple-sector mass spectrometer with BEB geometry was used for analysis. The apparatus has been described elsewhere.[7] In a typical experiment 15 μL of nitrile and 3 μL of $Fe(CO)_5$ are injected into a reservoir and permitted to flow into the ion source. The mass corresponding to the $Fe(RCN)^+$ ion[8] is selected and focused with the first magnet and the electrostatic analyzer. Collision gas (He, 2.0×10^{-5} mbar) is introduced in the collision chamber located in the third field free region, and fragments are analyzed by scanning the second magnet. All nitriles studied were either commercially available or, in the case of the labeled compounds, synthesized by known procedures and purified by gas chromatography. Their purity and both the location and label content were checked by ^1H NMR and electron impact mass spectrometry.

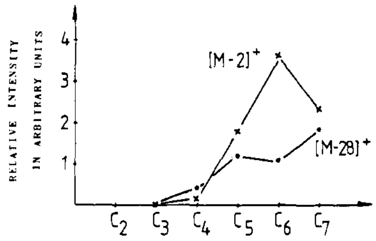

Figure 2. Relative intensities for losses of H_2 (x) and C_2H_4 (●) as a function of the chain length of linear nitriles (carbon numbers given include the CN carbon).

Table I.

precursor	neutrals lost	
$CH_3(CH_2)_4CD_2CN$	H_2[a]	C_2H_4[a]
$CH_3(CH_2)_2CD_2CH_2CN$	H_2[a]	C_2H_4[a]
$CH_3CD_2CH_2CH_2CN$	HD[b]	$C_2H_2D_2$[b]
$CH_3CH_2CD_2CH_2CH_2CN$	H_2[a]	C_2H_4[a]

[a] Loss of D-labeled neutrals is smaller than 0.1% relative to H_2 and C_2H_4. [b] Loss of H_2 and C_2H_4 is smaller than 0.1% relative to HD and $C_2H_2D_2$.

Results and Discussion

The reactions of Fe^+ with three linear nitriles (penta-, hexa-, and heptantrile) produce two major products, corresponding to the neutral loss of 2 and 28 mass units. Figure 1 shows a typical collisional activation (CA) mass spectrum with hexanitrile/Fe^+. In all three cases the $[M - 2]^+$ signal accounted for the base peak, followed closely in intensity by the $[M - 28]^+$ signal. The loss of 2 mass units can only arise from the loss of two hydrogen atoms and, for energetic reasons, presumably in the form of H_2. The loss of 28 mass units may hastily be interpreted as the loss of ethylene. However, due to the CA conditions, it could conceivably be due a loss of H_2 followed by the loss of CN through fragmentation. To resolve this question, the carbon of the cyano group was labeled with ^{13}C and examined. However, no loss of 29 mass units was observed, confirming that the loss of 28 mass units is, indeed, due to a loss of C_2H_4, presumably ethylene.

These results greatly differ from those observed for the reactions of alkenes[4a] and alkynes[4b] with bare Fe^+. In these systems, allylic or propargylic cleavages of either C–C or C–H bonds dominate. Hence, the neutral fragments lost always depend on the length of the carbon chain and can, in fact, be used to locate unambiguously the position of the C–C double bonds (and, in principle, C–C triple bonds).[8]

A systematic study of the chain-length effects on the formation of the $[M - 2]^+$ and $[Me - 28]^+$ ions shows the following (Figure 2): Both processes are absent for acetonitrile (C_2) and propionitrile (C_3).[10] They are first observed for the C_4 nitrile and remain high between C_5 and C_7. These results are a first indication of the selectivity of the reaction to remote carbons, reactivity being preferred for nitriles with at least five carbon atoms.

Deuterium labeling was performed to determine from which positions in the molecule the hydrogen and ethylene molecules originate (Table I). Labeling the C_2 and the C_3 positions produces no loss of deuterium label either in the hydrogen or in the ethylene. When the C_4 positions are labeled we observe both deuteriated and nondeuteriated losses, depending on the length of the carbon chain. For the C_6 nitrile no loss of the deuterium label was observed, indicating the preference of Fe^+ for activating the C_5 and C_6 positions. With the C_5 nitrile, only the loss of HD and $C_2H_2D_2$ is observed in the absence of other isotopic isomers. Formation of H_2 must therefore occur via 1,2-elimination involving

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(5) For selected reviews on the subject, see: (a) Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170. (b) Breslow, R. *Chem. Soc. Rev.* **1972**, *1*, 553. See also: (c) Kerb, U.; Stahnke, M.; Schulze, P. E.; Wiechert, R. *Angew. Chem.* **1981**, *93*, 89. (d) Breslow, R.; Maresca, L. M. *Tetrahedron Lett.* **1977**, 623.

(6) Similar behavior of metals to CH and CC activation has been reported earlier particularly by Tsarbopoulos et al. (ref 3e) and Burnier et al. (ref 3g). Reactions of metal ions with *unlabeled* nitriles were recently reported as a short communication at the 10th International Mass Spectrometry Conference (Swansea, 1985): Allison, J.; McElvany, S.; Radecki, B.; Tsarbopoulos, A. *Adv. Mass Spectrom.* **1985**, 799.

(7) Weiske, T. Ph.D. Thesis, Technical University, Berlin, 1984. Terlouw, J. K.; Weiske, T.; Schwarz, H.; Holmes, J. *J. Org. Mass Spectrom.* **1986**, *21*, 665.

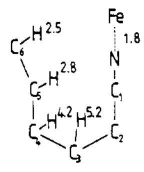
(8) The formation of $Fe(RCN)^+$ is very likely not to occur in a three-body process but rather to involve the reaction of $Fe(CO)_x^+$ ($x = 1, 2$) with RCN. Ligand substitution in the encounter complex leads to $Fe(RCN)^+$. It should be mentioned that by using double-resonance FTICR it was demonstrated that $Fe(alkyne)^+$ complexes are formed by the reaction of $Fe(CO)_x^+$ ($x = 1, 2$) with neutral alkynes: (a) Reference 4a,c. (b) Peake, D. A.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 115. Although reactions performed at 10^{-7} torr may not strictly apply at the high pressure (0.1 torr) used in the chemical ionization source and the reactions of nitriles are not necessarily identical with those of alkynes, we believe that the $Fe(RCN)^+$ species are formed by an analogous reaction sequence. Be this so or not, the *actual* ion formation mechanism (which cannot be uncovered by using our present methodologies) has *no* implications for the chemistry of the mass-selected $Fe(RCN)^+$ ions. Similarly, there is also experimental evidence that the reactivity of Fe^+ with larger molecules (in contrast to reactions with smaller ones, like H_2) is relatively insensitive to the electronic state of Fe^+ (see ref 12 in: Sonnenfroh, D. M.; Farrar, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3521).

(9) For leading references of the CA methodology, see: (a) Levsen, K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 509. (b) *Collision Spectroscopy*; Cooks, R. G., Ed.; Plenum: New York, 1978. (c) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77.

(10) The major product for C_2, C_3, and C_4 nitriles is simply the loss of the neutral nitrile, thus producing $[Fe]^+$.

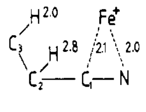
the C_4 and C_5 positions, consequently producing a π-adsorbed olefin. The loss of $C_2H_2D_2$ demonstrates that the same carbon positions which yield hydrogen atoms (C_4 and C_5) are also involved in the formation of ethylene, implying that the losses of hydrogen and ethylene are competing processes involving a common intermediate.

The preference for activating remote C–H bonds may be explained in terms of the coordination between Fe^+ and the CN group. Two types of coordination are conceivable, corresponding to end-on (**1**) or side-on (**2**), the latter being analogous to alkyne and alkene coordination. The fact that the products observed for the nitriles differ from those of either alkenes or alkynes already gives some indication of the difference between the coordination of Fe^+ to nitriles and to unsaturated hydrocarbons. The observed reactivity of the labeled compounds is further supported by the chain-length dependence of the system, both of which point to a type **1** coordination. The reactivity may thus be explained in *pure geometrical* terms.[11] For the side-on coordination (**2**), the hydrogen atoms attached to C_2 and C_3 are 2.8 and 2.0 Å from the Fe center, respectively. Interestingly, a class of organometallic compounds has recently appeared in the literature in which the metal center interacts with a C–H unit intramolecularly with M–H distances between 2.3 and 3.0 Å.[12] Hence, the relatively close proximity of the hydrogen atoms on these positions is consistent with the observed reactivity of both alkynes and alkenes. Conversely, for the end-on coordination (**1**), the corresponding distances to C_2 and C_3 are ca. 4.5 and 5.2 Å, respectively. The M–H distance becomes only significantly more favorable for hydrogen atoms attached to C_5 (2.8 Å) and C_6 (2.5 Å), in line with our observations.



"End-On"

1



"Side-On"

2

A quick survey of the coordinating behavior of nitriles to other metallic systems, such as bulk and cluster, also more or less points to a type **1** coordination. On bulk metals, the desorption activation energy of acetonitrile on nickel increases by 7.4 kcal/mol when the methyl is replaced by a strong σ-accepting substituent, e.g., CF_3.[13] On the other hand, when *tert*-butyl is used, which should strongly sterically interact with the surface in a type **2** coordination, only a minor change in activation energy is observed (14.2 and 13.5 kcal/mol, respectively). The X-ray study of the coordination of acetonitrile on Fe_3 clusters shows the nitrogen primarily coordinated to one Fe atom and the π-orbitals of the CN group to an adjacent Fe atom.[14] However, the interaction between acetylene and the same Fe_3 complex differs markedly from that of the nitrile. It remains to be seen how flexible the Fe^+ atom is from linearity. This will be the subject of future theoretical studies by our group.

We thus propose the mechanism for the elimination of hydrogen and ethylene from C5 nitrile/Fe^+ illustrated in Figure 3. Since the formation of both H_2 and C_2H_4 originates from the same positions on the molecule, as shown by the labeling experiment, and seems to rise synchronously with the chain length (with the exception of C_6 nitrile), both processes must therefore be proceeding in competition through the same intermediate (Figure 3). The intermediate that we propose (**4**) involves the initial activation of a single C–H bond forming a cyclic species which has often been proposed in other gas-phase organometallic reactions, particularly with ketones and alcohols.[6] From **4** there are two possible routes to explain the observed products: (a) β-hydride shift to produce the π-adsorbed olefin (**7**), which then undergoes reductive elimination to produce HD, and (b) C–C bond cleavage forming **6**, which eventually eliminates $C_2H_2D_2$.

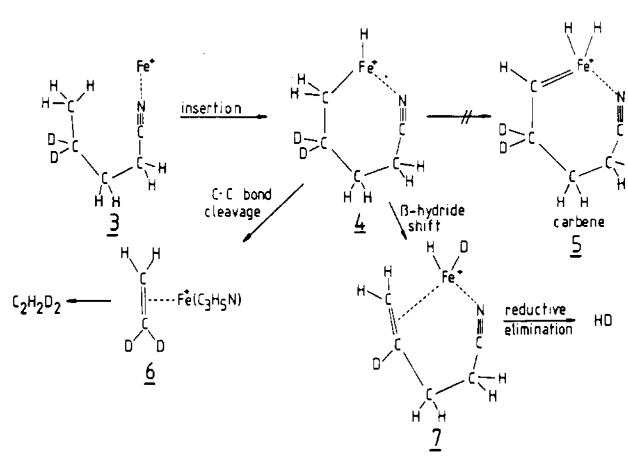


Figure 3. Proposed mechanism for the reaction of Fe^+ atoms with linear nitriles.

The proposed mechanism is supported by a further CA study of the $[M - 28]^+$ ion generated from the C_7 nitrile/Fe^+ species. The collisional activation spectrum of this species again shows loss of ethylene and hydrogen as major products. This is to be expected since the $[M - 28]^+$ species of C_7 nitrile should be identical with that of the $[M]^+$ spectra of the C_5 nitrile/Fe^+ system. Furthermore, the CA spectrum of the $[M - 28]^+$ ion generated from C_5 nitrile/Fe^+ does *not* show intensities corresponding to losses of either ethylene or molecular hydrogen, in agreement with the observations for C_3 nitrile/Fe^+.[15]

Conclusion

The reaction of Fe^+ with linear nitriles results in an end-on complexation that effectively hinders activation of CH and CC bonds near the CN functionality. For penta-, hexa-, and heptanitrile, this means activation of the terminal ethylene group almost exclusively. Principally, this type of remote functionalization should not be limited to the gas phase but should also be applicable to solution chemistry. We are currently studying the effects of yet longer, specifically labeled nitriles to the products and also plan to investigate the effects of different metal ions to the site selectivity of the process.

Acknowledgment. The generous support of our work by the Deutsche Forschungsgemeinschaft (Projekt Schw 221/6-4) and the Fonds der Chemischen Industrie is gratefully acknowledged. C.B.L. wishes to thank the Alexander von Humboldt Foundation for providing a postdoctoral fellowship. We are indebted to Dr. Thomas Weiske, Berlin, for technical assistance.

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(11) Geometries are calculated from a combination of X-ray data (see ref 14) and geometrical molecular models.

(12) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Saillard, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(13) Wexler, R. M.; Mueterties, E. L. *J. Phys. Chem.* **1984**, *88*, 4037.

(14) Andrews, M. A.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7260.

(15) A referee has suggested that, because of the presence of a signal due to loss of C_2H_5 from RCN/Fe^+ (Figure 1), the process of ethylene elimination may not involve intermediate **4** but rather may follow the conventional reaction sequence, i.e., oxidative insertion of Fe^+ into the CH_3CD_2–C bond, to generate an ethyl-Fe^+–alkyl intermediate, followed by β-hydrogen shift and loss of ethylene. We disagree with this suggestion on the following grounds: (i) This mechanistic scheme could not account for the fact that, irrespective of the chain length, *ethylene* is the preferred olefin eliminated. In fact, preliminary studies on yet longer alkyl nitriles (C_8–C_{10}) confirm that ethylene and hydrogen losses from the RCN/Fe^+ complexes are the dominating reactions. If the reaction were to proceed analogously to those involving alkenes and alkynes, then a similar chain-length behavior should be observed. This is not the case. (ii) The products observed via loss of C_2H_4 from the higher nitriles, i.e., C_5 nitrile/Fe^+ generated from C_7 nitrile/Fe^+, give rise to *identical* CA mass spectra. If C_2H_4 loss would proceed via C–C insertion, followed by β-hydrogen transfer, the resulting *hydrido*–Fe^+ complex is expected to show a different reactivity. (iii) The observed parallel behavior for H_2/C_2H_4 losses as a function of chain length points to a common intermediate. Further examples, demonstrating that C–H insertion of a complexed metal ion in the gas phase *precedes* C–C insertion, are described in: (a) Schulze, C.; Weiske, T.; Schwarz, H. *Chimia* **1986**, *40*, 362. (b) Schulze, C.; Schwarz, H.; Peake, D. A.; Gross, M. L. *J. Am. Chem. Soc.*, submitted for publication.