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Reactions of monosubstituted alkanes with bare metal ions. An effort toward a more unified picture for the gas-phase chemistry of R–X molecules

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CONTENTS

ABBREVIATIONS

B	magnetic field
CI	chemical ionization
CID	collision-induced dissociation
Cp	η^5-C_5H_5
$D^0(A^+{-}B)$	bond dissociation energy of AB^+ into A^+ and B
DR	double resonance
E	excitation plates
FAB	fast atom bombardment
FTICR	Fourier transform ion cyclotron resonance
i-Bu	$(CH_3)_2CHCH_2-$
ICR	ion cyclotron resonance
i-Pr	$(CH_3)_2CH-$
KIE	kinetic isotope effect

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LD/I	laser desorption/ionization
MS	mass spectrometer
n-Bu	$CH_3(CH_2)_3-$
R	receiver plates
RRKM	Rice–Ramsperger–Kassel–Marcus (theory)
sec-Bu	$C_2H_5CH(CH_3)-$
T	trapping plates
t-Bu	$(CH_3)_3C-$
t-Pent	$C_2H_5(CH_3)_2C-$
TS	transition state

A. INTRODUCTION

Gas-phase organometallic chemistry has developed into an actively pursued field of research, as may be seen from the rapidly growing number of publications on the subject. A comprehensive review has been published recently [1] (for an earlier review, see ref. 2), and there is also already a considerable number of more specialized articles [3–10]. This interest is due to the fact that the study of reactions in the gas phase, or more precisely in the vacuum of a mass spectrometer, has some unique advantages otherwise unattainable. Nowhere else can highly unsaturated, namely bare ("naked"), metal ions be produced and reacted with some substrates under well-defined conditions. All disturbing influences due to solvent and counter ions are absent, and thus, intrinsic metal-ion properties are accessible to the investigator. Ligand effects may be probed by means of ligated metal ions (e.g. FeO^+, $NiCH_3^+$, $Co(\eta^5\text{-}C_5H_5)^+$) that are either formed starting from a bare metal ion or from a suitable precursor complex [1].

Early studies were mainly concerned with alkane activation* by metal cations, M^+, because of the industrial importance of activating these unreactive C–H and C–C bonds. It was found that only certain transition-metal ions were able to activate alkanes despite the fact that all of them were highly coordinatively unsaturated [1]. The early transition-metal ions Sc^+, Ti^+, and V^+, as well as most of the second- and third-row ions, mainly attacked the stronger C–H bonds and gave rise to (multiple) dehydrogenations or loss of hydrogen molecules together with other small neutral particles. Cr^+, Mn^+, Cu^+, and Zn^+ were unreactive toward alkanes, which is due to their filled or half-filled d shells. With their d^5, d^5s^1, d^{10}, or $d^{10}s^1$ ground states, these ions are unable to undergo the oxidative additions necessary to activate the substrates. Finally, Fe^+, Co^+, and Ni^+ exhibited a versatile chemistry with the different alkanes, and C–H as well as C–C cleavages were observed.

Subsequently, interest also shifted to alkenes and alkynes, and while for these

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* The condensed phase approach with homogeneous catalysts is reviewed in ref. 11.

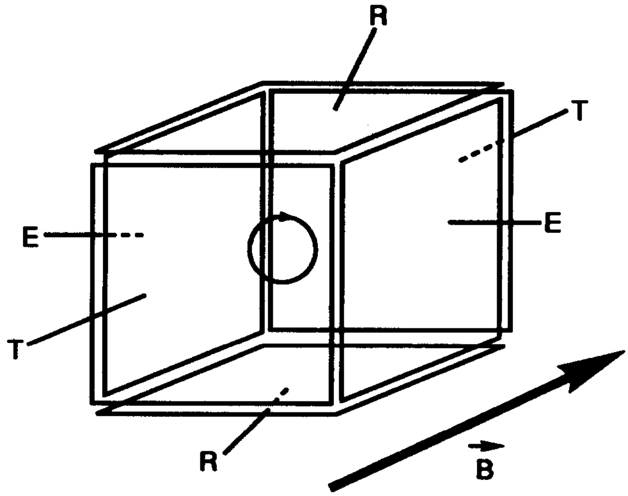
substrates broad generalizations on behalf of the metal ions' characteristics are no longer warranted, it can still be stated that two major classes of behavior emerged. The chemistry was either dominated by allylic or propargylic C–C activations, or the multiple bond merely served as a coordination site for the metal ion, and insertion proceeded into remote bonds. This so-called "remote functionalization" will be discussed in more detail later. Many other classes of substrate were studied, from which this review will focus on the reactions of bare metal ions M^+ with monosubstituted alkanes RX. For overviews about other types of molecule [1], reactions of metal-containing anions [3,12], or cluster studies (for reviews, see ref. 13), the reader is referred to the cited literature.

B. INSTRUMENTATION

Mainly three types of instrument have been used in the studies to be described. Most often, ion cyclotron resonance (ICR) (for reviews, see ref. 14) or the more advanced Fourier transform ion cyclotron resonance (FTICR) spectrometers (for recent reviews, see ref. 15) were employed as they are ideally suited for the study of ion/molecule reactions. Only the FTICR technique, as the currently favored method, will be described briefly. Metal ions are usually formed by laser desorption/ionization (LD/I) [16] as this conveniently matches the pulsed nature of the FTICR experiment. The ions can be formed either inside or outside the FTICR cell; in the latter case, they have to be transferred into the cell by means of quadrupole or electrostatic potentials. The cell (Scheme 1) is located in a strong magnetic field B (1–7 T) which forces the ions on circular paths perpendicular to B; small electric potentials (1–2 V) on the trapping plates T further restrict the ion motion in the field direction. The ions can thus be stored in the cell for extended periods of time (milliseconds to hours). The substrate is leaked or pulsed into the cell, and after a certain reaction delay, products are analyzed by simultaneous excitation of the ions, which are centered in the middle of the cell, to larger orbits with the help of radiofrequency pulses applied to the excitation plates E. Upon circulating, they induce an image current in the receiver plates R. This signal is a superposition of all cyclotron frequencies, which depend on the ions' mass-to-charge ratios, and Fourier transformation thereof provides a mass spectrum of the products formed.

Double resonance (DR) techniques allow the identification of a precursor ion to a given product ion by either constantly ejecting a single ion, increasing its cyclotron radius until it strikes the cell boundaries, or by isolation, ejecting all ions except for one [17]. Structural information about the ions is available from low-energy collision-induced dissociation (CID) by accelerating an isolated ion into a stationary target gas, usually argon [18].

The second type of instrument are ion beam apparatuses [19]; two different versions have been employed, guided and crossed-beam spectrometers. The ions are produced in an ion source, extracted therefrom, the reagent ion is mass-selected, usually with a magnetic sector, decelerated to a well-defined collision energy by an

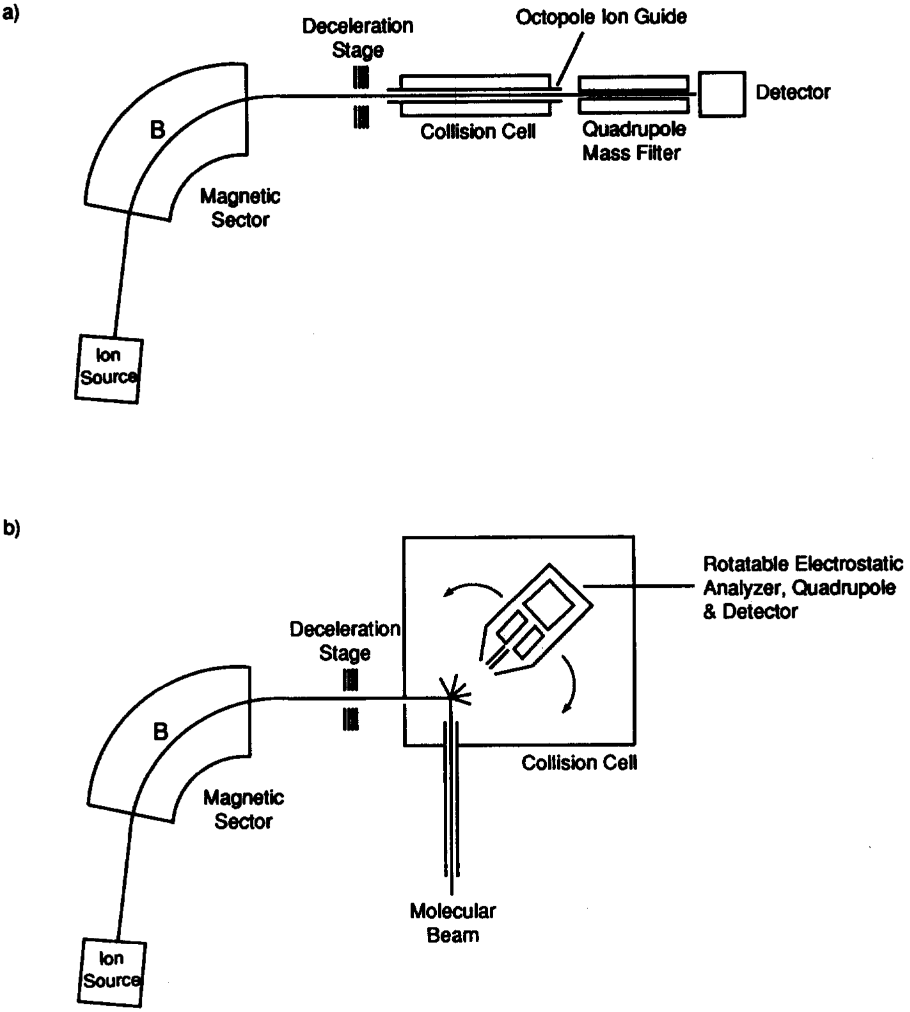


Scheme 1. Schematic drawing of a cubic FTICR cell, located in a magnetic field of strength B (1–7 T in modern instruments). T are the trapping, E the excitation, and R the receiver plates.

electrostatic retarding field, and focussed into the collision region. In guided ion-beam instruments (Scheme 2(a)), the ions are guided through the collision cell, containing the reagent gas, by an octopole (see, for example, ref. 20). The products are analyzed by a quadrupole mass filter and finally detected with a scintillation ion counter. In the crossed-beam version (Scheme 2(b)), the ion beam intersects a perpendicular molecular beam produced by supersonic expansion, and products are detected with a rotatable electrostatic analyzer, quadrupole, and scintillation counter (see, for example, ref. 21). By scanning the area around the collision center in the plane of the beams, a contour map with the angle and recoil-energy data for every product as well as scattered reactant ions is measured. With both methods, the raw data have to be treated with deconvolution functions to obtain quantitative information.

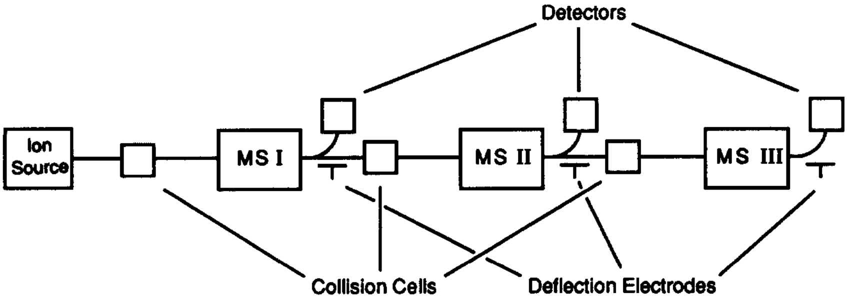
Similar to guided ion-beam instruments is the use of triple-quadrupole mass spectrometers where Q_1 is used for selection of the reactant ion, Q_2 is operated in the "RF only" mode and contains the reactant gas, and Q_3 is used for product-ion identification (see, for example, ref. 22).

The last approach to gas-phase organometallic chemistry employs sector mass spectrometers [23] and differs from the other two methods in a very significant aspect, that the starting point is not a bare metal ion but an organometallic complex whose metastable or collision-induced decompositions are studied instead. These complexes are formed in the ion source of the instrument (Scheme 3), and most conveniently, a high-pressure chemical ionization (CI) source is used. Ionization of a ca. 1:5 mixture of an appropriately volatile organometallic compound (e.g. $Fe(CO)_5$ or $Co(CO)_3NO$) with the substrate often gives rise to 1:1 adduct complexes of the metal ion with the substrate, which are formed by various ion/molecule reactions



Scheme 2. (a) Schematic drawing of a guided ion-beam instrument where the precursor ion is formed in the ion source, selected with a magnetic sector B, decelerated, and collided in the collision cell with a neutral reagent gas. Ionic products are analyzed by scanning of the quadrupole mass filter. (b) In a crossed-beam instrument, the decelerated precursor ion intersects the molecular beam of the reagent gas at right angles, and scattered products are detected with a rotatable unit consisting of an electrostatic analyzer, a quadrupole, and a detector.

inside the source. Alternatively, such complexes may also be formed by the "fast atom bombardment (FAB) method" [24], where a target of an inorganic salt is bombarded with fast Xe atoms, and liberated metal ions or clusters react with the simultaneously present substrate, which is leaked into the ion source. Complexes formed by either ionization method are extracted from the source, accelerated, and mass-selected with the first mass spectrometer (MS I) which can be either a magnetic



Scheme 3. Schematic drawing of a triple-sector instrument with various collision cells and detectors in which the metastable or collision-induced decompositions of adduct complexes, formed in the ion source, can be studied.

or an electrostatic sector or even both. In a field-free region of the instrument their unimolecular decompositions (metastable ions, MI [25]) or high-energy collision-induced decompositions (for reviews, see ref. 26) are studied by scanning of MS II. Structural information about a product ion is achieved by selection of the respective ion with MS II and CID in the collision cell in front of MS III. Detection is accomplished with secondary electron multipliers available after each sector.

It is not self-evident that ion/molecule reactions of bare metal ions M^+ with neutral substrates AB in an FTICR instrument and metastable-ion studies on $M(AB)^+$ adduct complexes should yield similar results, but comparisons have shown that, if several restrictions are kept in mind, product distributions are usually fairly similar, and good agreement is found for label distributions in individual reactions [27–32]. Similar comparisons have also been drawn between ion-beam investigations and MI and CID spectra of transition-metal ion/alkane complexes [33]. Care is, however, needed to show that $M(AB)^+$ ions are indeed formed in the sector studies. It will be shown later that, under certain conditions, isomeric $M(A)(B)^+$ complexes may also be generated. Needless to say, their selection would lead to erroneous conclusions.

C. REACTIONS OF ALKALI AND OTHER MAIN-GROUP IONS

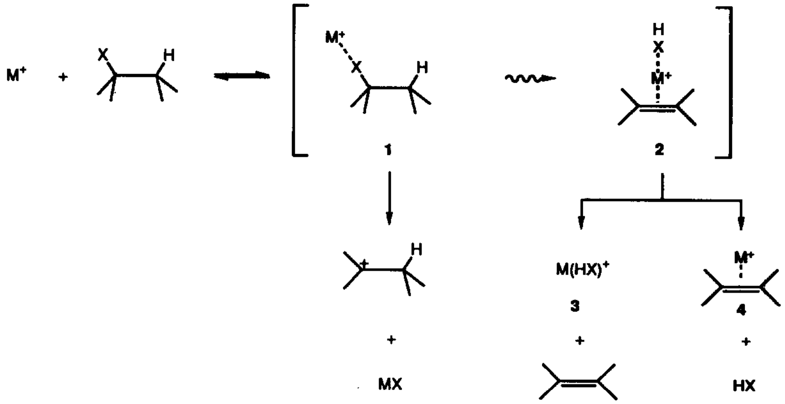
In 1975, Beauchamp and co-workers reported that Li^+, generated by thermoionic emission [34] in an ICR cell, reacted with several alkyl halides RX (X = Cl, Br) while no reactions were observed with Na^+ or K^+ [35]. In addition to the anticipated halide abstraction (1), cleavage into HX and alkenes was also observed (reactions (2) and (3)).

$$M^+ + C_nH_{2n+1}X \rightarrow C_nH_{2n+1}^+ + MX \quad (1)$$

$$\rightarrow M(HX)^+ + C_nH_{2n} \quad (2)$$

$$\rightarrow M(C_nH_{2n})^+ + HX \quad (3)$$

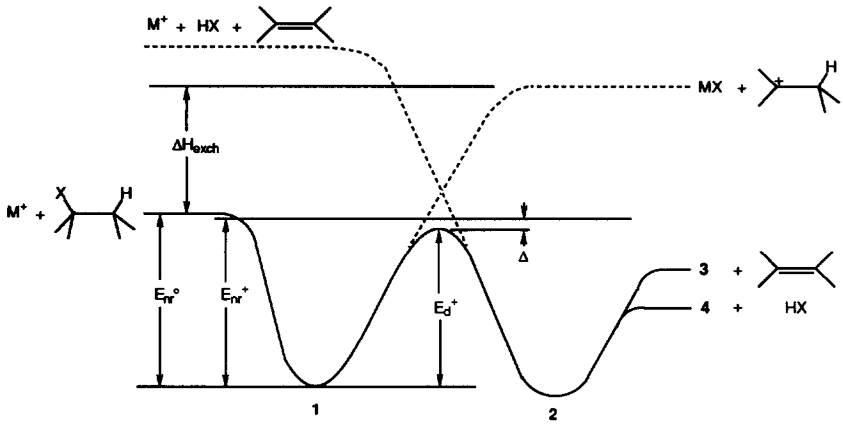
In accordance with thermochemical estimates, reaction (1) was only observed when it was exothermic [35,36]. The use of $(CD_3)_2CHCl$ revealed the exclusive operation of a 1,2-elimination in reactions (2) and (3) [35], and Allison and Ridge were able to find reaction (3) for Na^+ and tertiary chlorides and reactions (2) and (3) for Li^+ and *t*-BuOH [37,38]. Ethyl fluoride was also observed to react with Li^+ accordingly, and both cleavage products were formed [39]. It was proposed that association of the alkali ion to the halide leads to the formation of a chemically activated species which may dissociate to an alkali halide and a carbenium ion (Scheme 4) [35]. Rearrangement of this intermediate **1** to **2** precedes the competitive ligand loss to afford **3** and **4**. Later, this mechanism was termed "dissociative attachment" or was simply referred to as Lewis-acid chemistry and was invoked for other substrates RX, in particular for alcohols. It was, however, not until 1989 that the details of the rearrangement of **1** to **2** were determined [40] and explained in terms of an ion/dipole mechanism [8(c),(d),28,41]. As these studies were done with transition-metal ions, the discussion is deferred for now.



Scheme 4. Proposed mechanism [35] for the reactions of alkali-metal ions with alkyl halides and alcohols.

The potential-energy surface for reactions (2) and (3) has been described as shown in Scheme 5. The initial collision complex **1** is separated from the reactants by the ion/dipole attraction and the well depth is E^0_{nr}. Due to the simultaneous occurrence of tight and orbiting transition states [42], however, the transition state for the dissociation of **1** corresponds to the slightly smaller activation energy E^+_{nr}. E^+_d is the transition-state energy for the isomerization to **2**. The position of **3** and **4** depends on the respective binding energies of HX and the alkene and may be reversed.

By measuring the branching ratio for **3** and **4** relative to the non-reactively scattered M^+ with a crossed-beam apparatus, the quantity Δ may be obtained by employing statistical RRKM calculations. By this means, Creasy and Farrar determined Δ for the reaction of Li^+ with *tert*-butyl alcohol as (-1.6 ± 0.7) kcal mol^{-1}



Scheme 5. Energy profile for the mechanism in Scheme 4.

[43] which implies that the barrier for isomerization of $[\text{Li}(t\text{-}C_4H_9OH)^+]^*$ is *larger* than the activation energy for redissociation to reactants. As the difference between E^0_{nr} and E^+_{nr} is unknown, it was concluded that E^+_d is equal to E^0_{nr} within $\pm 1.15\ \text{kcal mol}^{-1}$. Distinction between direct elastically scattered Li^+ and Li^+ ejected non-reactively from the collision complex was achieved from a polar flux contour map, which at small angles showed a high-energy peak and a low-energy one at larger angles; at intermediate angles, bimodal distributions were observed. Sampling the first well on the reaction coordinate, the Li^+ collision energy is thermalized and this results in a shift to lower energies upon reverting to educts. Results for $i\text{-}C_3H_7Cl$, $i\text{-}C_3H_7Br$, and $n\text{-}C_3H_7Cl$ reacting with Li^+ indicated that E^+_d increased in the order of citation [44], and for all three halides the barrier was lower than for $t\text{-}C_4H_9OH$. There was no correlation between E^+_d and ΔH_{exch}, the enthalpy for the exchange of the chloride ion between Li^+ and the carbenium ion R^+. It was therefore concluded that the transition state at the isomerization barrier depends not only upon the development of a positive charge on carbon but also upon other factors. Any correlation [45] could have been interpreted as the result of a curve crossing, as indicated in Scheme 5 and initially proposed by Allison and Ridge [38]. With decreasing ΔH_{exch}, this crossing point would have been lowered and hence led to a reduced barrier between the two wells.

Scheme 4 has also been invoked for the reactions of Al^+ [46–48], Ga^+ [47], In^+ [47], and Mg^+ [48,49] with alcohols and alkyl halides. In cases where reactivity was observed, reactions (1)–(3) were the only processes noted. For alcohols, adduct formation was occasionally seen too; these reactions could either proceed by a bimolecular pathway through infrared stabilization of the internally excited encounter complex $[M(ROH)^+]^*$ or by stabilization of the latter through a collision with a further neutral molecule. Al^+ does not react with CH_3Cl or CH_3Br [46–48], but for ethyl and isopropyl chloride, reactions (1)–(3) were observed in an ion-beam study [46]. Under ICR or FTICR conditions, however, the ethyl halides C_2H_5X ($X = Cl, Br, I$) did not give rise to any products, and other alkyl chlorides and bromides exclusively afforded R^+ and AlX according to reaction (1) [47,48]. With CH_3OH, only adduct formation was observed for Al^+, but C_2H_5OH formed AlH_2O^+ [47,48] in a 1,2-elimination, as evidenced by the production of $AlHDO^+$ from CD_3CH_2OH [47]. Higher alcohols reacted by hydroxide transfer (1) and formation of AlH_2O^+ (2); alkene complexes (3) were absent [47,48]. Ga^+ and In^+ showed a very similar behavior with only slight differences observed [47]. While methanol did not give rise to any products, the higher alcohols exclusively formed adduct complexes $M(ROH)^+$. Smaller alkyl chlorides and bromides were also unreactive, but halide transfer (1) and loss of HX (3) were found for larger halides. In contrast to the alcohols, reaction (2) was absent for both metal ions in case of the halides. The same applies to the reactions of Mg^+, where (1) and (3), but not (2), were observed with alkyl chlorides and only reaction (2) for some higher alcohols. Smaller alcohols only afforded adduct complexes with Mg^+ [48,49].

The products for reactions (2) and (3) usually undergo secondary and higher-order reactions with the substrate RX; a typical sequence is given in reactions (4)–(9) for Li^+ and t-BuCl [38].

$$Li^+ + t\text{-}C_4H_9Cl \rightarrow Li(C_4H_8)^+ + HCl \tag{4}$$

$$Li(C_4H_8)^+ + t\text{-}C_4H_9Cl \rightarrow LiC_4H_9Cl^+ + C_4H_8 \tag{5}$$

$$\rightarrow Li(C_4H_8)_2^+ + HCl \tag{6}$$

$$LiC_4H_9Cl^+ + t\text{-}C_4H_9Cl \rightarrow Li(C_4H_8)(C_4H_9Cl)^+ + HCl \tag{7}$$

$$Li(C_4H_8)_2^+ + t\text{-}C_4H_9Cl \rightarrow Li(C_4H_8)(C_4H_9Cl)^+ + C_4H_8 \tag{8}$$

$$Li(C_4H_8)(C_4H_9Cl)^+ + t\text{-}C_4H_9Cl \rightarrow Li(C_4H_9Cl)_2^+ + C_4H_8 \tag{9}$$

Double-resonance experiments with a mixture of $t\text{-}C_4H_9Cl$ and $t\text{-}C_4D_9Cl$ revealed that the neutral product in (7) originated from both the neutral and the ionic reagent. This could be demonstrated by making use of the naturally occurring $^{35}Cl/^{37}Cl$ isotopes and led to the conclusion that a symmetrical intermediate of the type $[Li(C_4H_9{}^{35}Cl)(C_4D_9{}^{37}Cl)^+]^*$ was involved.

The extensive chemistry of the initially formed complexes was used in studies aimed at the determination of binding energies of different ligands to Li^+ [50,51]. The method has also been used for Mg^+ [48,49], Al^+ [48,52], and Mn^+ [53] and is based on the equilibrium in (10) (for a summary of the findings, see ref. 54).

$$ML_1^+ + L_2 \rightleftharpoons ML_2^+ + L_1 \tag{10}$$

Measurement of the equilibrium constant for reaction (10) allows determination of ΔG for the process and construction of a relative scale of ligand binding energies for M^+. Experimentally, this is most conveniently done by reaction of M^+ with a mixture of two ligands in an ICR or FTICR instrument. If the absolute binding energy of one ligand can be determined experimentally or theoretically, the whole scale can be tied to that value and converted to an absolute scale.

Analogously, the equilibrium in reaction (11) has been used to derive relative two-ligand bond dissociation energies for M = Mg [49], Co [55], Ni [56], and Cu [57]*.

$$M(L_1)_2^+ + 2L_2 \rightleftharpoons M(L_2)_2^+ + 2L_1 \qquad (11)$$

Some general conclusions that were derived are increased binding energies with increasing substitution, i.e. propene < isobutene, methanol < ethanol, and often, namely for softer acids, upon going down in the periodic table, i.e. alkyl chlorides < alkyl bromides, alcohols < thiols. There are, however, many exceptions to the latter generalization. If the binding energies of M_1^+ to different ligands L, $D^0(M_1^+{-}L)$, were correlated with those of another metal ion M_2^+, $D^0(M_2^+{-}L)$, linear relationships resulted for similar ligands such that, for instance, oxygen bases fell on one line and sulfur bases on another. The offsets and the slopes of these lines were interpreted in terms of relative hardness and softness of the metal ions and as indications for the $M^+{-}L$ bond distances. For Co^+, Ni^+, and Cu^+, synergistic effects have been evaluated by comparison of mixed complexes $M(L_1)(L_2)^+$ with $M(L_1)_2^+$ and $M(L_2)_2^+$ [58,59].

D. REACTIONS OF TRANSITION-METAL IONS

(i) Nitriles and isonitriles

While it will be shown later that some transition-metal ions behave superficially or in fact analogously to the main-group ions just discussed, in many cases a completely different chemistry is encountered. A particular prominent example is their ability to react by "remote functionalization".

This mechanism was first discovered by Schwarz and co-workers [8,60] and so termed to point out the analogy to Breslow's studies on biomimetic synthesis [61]. The initial interaction of a transition-metal ion M^+ with a monosubstituted alkane RX leads to a coordination at the functional group X. A strong bond between M^+ and X–R will efficiently prevent (for geometric reasons) the metal ion from undergoing an insertion into any of the C–H or C–C bonds in the proximity of X. As it is still possible to interact with remote bonds that are accessible by folding back the alkyl chain, oxidative addition occurs at positions that are separated by several methylene groups (at least three or four) from X. For substrates of an

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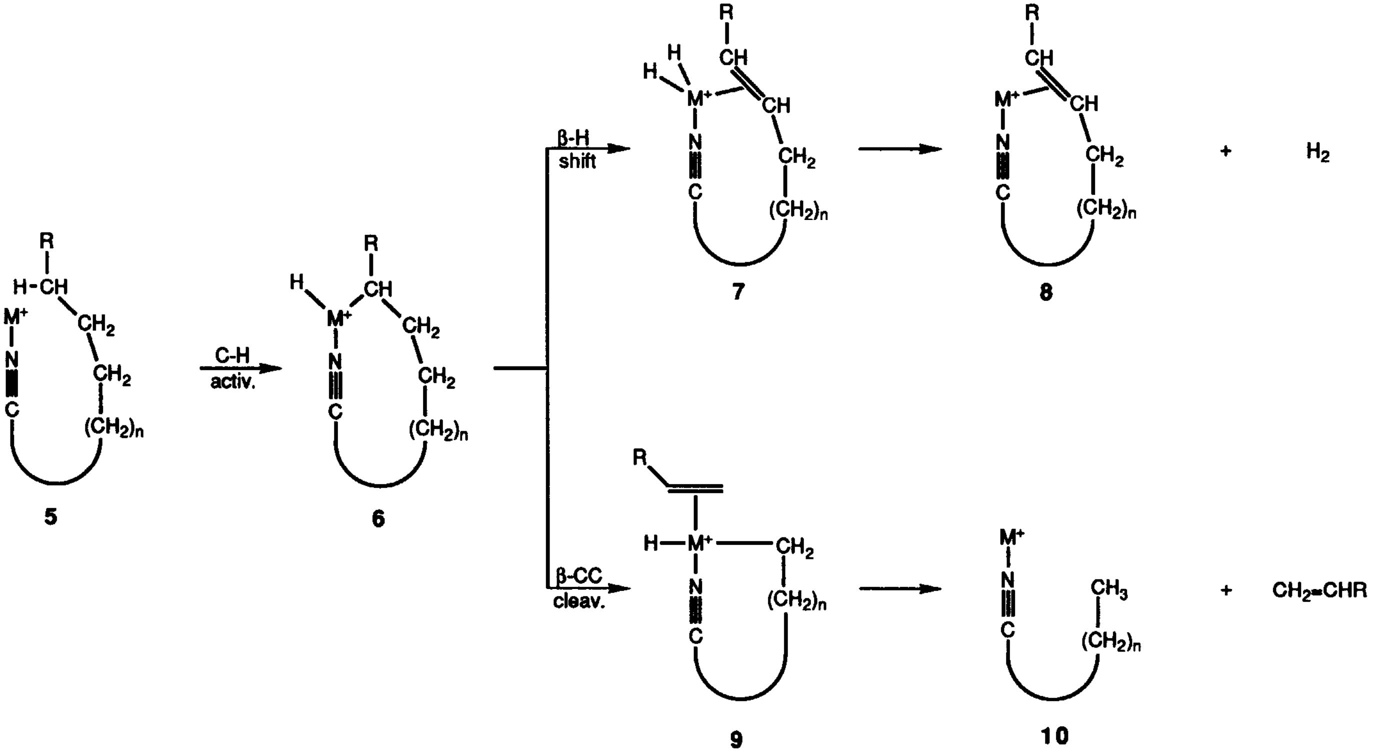
* The transition-metal ions have been included in this section as no mechanistic aspects are involved in the determination of the bond dissociation energies and no behavior different from main-group ions is encountered.

intermediate length, the selective activation of a C—H bond of the terminal methyl group is observed (Scheme 6, R = H), and the resulting intermediate **6** will undergo competitively either a β-hydrogen shift or cleavage of the β C—C bond. Reductive elimination of H_2 from **7** furnishes the ω-unsaturated complex **8**, while alkene loss from **9** is accompanied by a rearrangement to the shortened ligand in **10**. That indeed **10**, as opposed to a complex analogous to **6**, is formed, was shown by CID on the alkene-loss products [60,62] and by the labeling distributions of consecutive reactions [41,63,64]. In the former experiments, an MS/MS/MS spectrum of the alkene-loss product is compared with the MS/MS spectrum of an authentic $M(RX)^+$ complex. FTICR as well as sector instruments can be used for the comparison; in the former case, M^+ is isolated first (MS^1), reacted with R'X whereupon the alkene-loss product is isolated (MS^2), which is finally subjected to low-energy CID. In sector instruments, the $M(R'X)^+$ complex is isolated with MS I, undergoes metastable alkene loss, and MS II is used to isolate this product whose high-energy CID spectrum is obtained by scanning of MS III. The reference complex $M(RX)^+$ is formed in the ion source from M^+ and RX and should be studied with a reduced acceleration voltage to account for the fact that the alkene-loss product has a lower kinetic energy than its parent ion. But although identical spectra were obtained in one case where this technique was employed [65], the result was interpreted in terms of an inserted structure. In the labeling studies, alkene losses from ketones or secondary nitriles resulted in shortened ketones or nitriles where both sides were subsequently attacked.

The initial discovery of the remote functionalization mechanism was due to the rapid increase in the H_2- and C_2H_4-loss products for *n*-alkanenitriles reacting with Fe^+ [60]. Labeling of selected positions with ^2H substantiated the mechanism (Scheme 6) as the origin of the neutrals were the $\omega/(\omega-1)$ positions at the chain termini. No other products than from ligand detachment, loss of the complete ligand with concomitant formation of M^+, were observed in cases where remote functionalization was impossible due to the shortness of the alkyl chain. Going over to longer chain nitriles showed that eventually internal positions were also activated ($R = CH_3, C_2H_5, \ldots$), which led to the production of higher alkenes ($C_3H_6, C_4H_8, \ldots$) in addition to hydrogen from internal, but still remote, methylene groups [66]. The mechanism is not only restricted to Fe^+; Co^+ [66–68] and Ni^+ [68,69] were also found to react with nitriles by remote functionalization. In general, they showed a very similar behavior, except that Fe^+ seemed to have a preference for the activation of a C—H bond at C_8 while Co^+ and Ni^+ showed maximum reactivity at C_7. This difference was ascribed to slightly different coordination geometries; $d \rightarrow \pi^*$ back-bonding leads to a bent $CH_2CN{-}M^+$ arrangement so that methylene groups closer to the cyanide group may be reached more easily [69]. In theoretical studies, however, it is mostly found that transition-metal ions show only negligible back-bonding [7,70,71].

While in metastable-ion spectra C_nH_{2n+2} losses were either absent or negligible



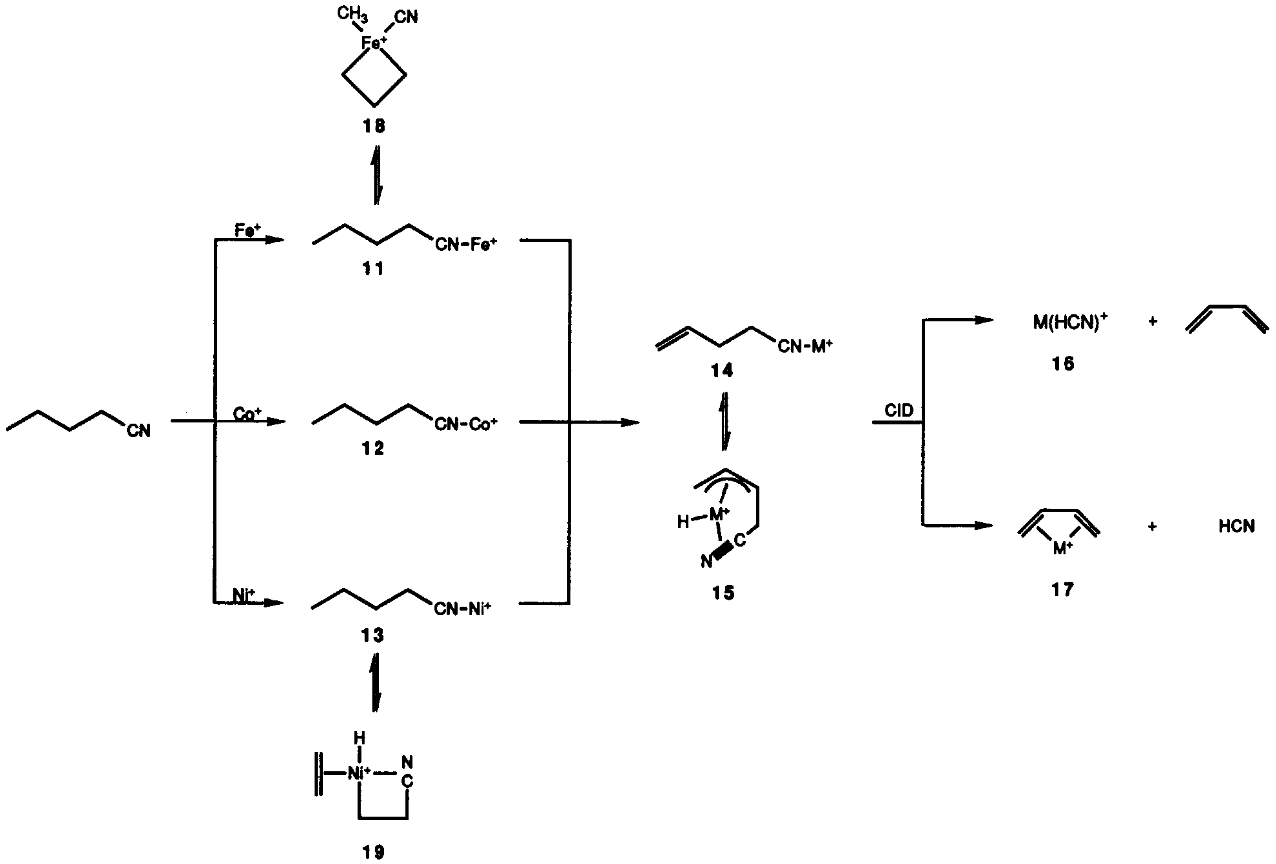
Scheme 6. Generalized mechanism for the "remote functionalization" of distant C–H bonds by bare transition-metal ions M^+, complexed to the functional group X of the organic substrate.

for linear nitriles [41,68], upon collisional activation of M(RCN)$^+$ complexes, formal losses of alkanes were observed [66,68]. ^{2}H-labeling and MS/MS experiments indicated that for Co$^+$ alkanes were indeed formed by C—C activation followed by β-hydrogen shift and reductive elimination [66]. For Fe$^+$, however, this applies only for the loss of CH_4 while other "C_nH_{2n+2}" losses were due to consecutive loss of H_2 and alkenes [66]. Allylic C—C insertion in the dehydrogenation product precedes β-hydrogen shift and alkene dissociation. This mechanism could be further substantiated by comparison with the reactions of alkenenitriles, which showed the same reaction already in metastable-ion spectra [72]. A different explanation was advanced for the C_nH_{2n+2} ($n = 4, 5$) losses observed upon reaction of Fe$^+$ with 8,8-dimethyl nonanenitrile [65]. Here, it was assumed that intact alkanes were formed by C—C insertion/β-hydrogen shift/reductive elimination. The choice of this particular nitrile was stimulated by the preference for insertion into $C_{(7)}$—H or $C_{(8)}$—H that Fe$^+$ had revealed earlier [60,66,69]. The system was designed as a test for β-CH_3 shifts, which could have been feasible after $C_{(7)}$—H insertion of Fe$^+$. Although CH_4 was formed as the main product, ^{2}H labeling revealed that it was actually due to insertion into one of the C—C bonds of the *t*-Bu group followed by β-H shift from C(9) (90%) or C(7) (10%) and reductive elimination. Also, hydrogen and isobutene were formed according to Scheme 6 (CH_2=$C(CH_3)_2$ in place of CH_2=CHR). In contrast to this study, methane loss induced by Fe$^+$—Ni$^+$ from the related compounds 3-methyl butanenitrile and 4-methyl pentanenitrile was ascribed to C—H insertion followed by β-CH_3 shifts [68]. Loss of hydrogen and propene from these substrates, the only other processes observed besides ligand detachment in the MI spectra, was, however, also explained by remote functionalization along the lines of Scheme 6.

As already mentioned, if the alkyl chain is too short for the operation of the remote functionalization mechanism, other processes such as ligand detachment can compete. To test the limits of the mechanism as well as the influence of the metal ions, *n*-pentanenitrile was studied with Fe$^+$ [73], Co$^+$ [62], Ni$^+$ [62], and Cu$^+$ [74]. The four metal ions behaved quite differently with the substrate; for Fe$^+$—Ni$^+$, different amounts of cleavage products were observed while Cu$^+$ was unreactive in the respect that only adduct formation was seen. The adduct was completely absent for Fe$^+$ and a minor product for Co$^+$ (7%) and Ni$^+$ (11%). Cu$^+$ possesses a closed-shell d^{10} configuration and is therefore unable to undergo oxidative addition reactions. To circumvent this problem, it often reacts via an ion/dipole mechanism, as will be shown in detail later, but in cases where this alternative is excluded by energetic reasons, adduct formation is the only possibility remaining. The inability of Cu$^+$ to activate C—H or C—C bonds is also evident from other studies with linear nitriles [27,75–78]. Under ICR or FTICR conditions, the adduct complex was the only product in all cases [27,74,76–78] while no products were seen in metastable-ion spectra [75]. Upon collisional activation of the Cu(RCN)$^+$ complexes, some fragment ions were observed, viz. CuHCN$^+$, $CuC_2H_2N^+$, and $CuC_3H_3N^+$ [27,75]. Although originally different structures and mechanisms were proposed [75], later studies on related systems suggest as more likely that the first ion is the hydrogen cyanide complex HCN–Cu^+ formed by the ion/dipole mechanism (see below) while the latter two arise by simple radical losses in the course of the CID process and not by oxidative addition. $CuC_2H_2N^+$ is probably due to simple C–C cleavage in R–CH_2CNCu^+ and $CuC_3H_3N^+$ by either R• loss from R–$CH_2CH_2CNCu^+$ followed by rapid H• loss, or by the reversed sequence, first H• then R• loss. In both cases a stable acrylonitrile complex is the final product.

In contrast to Cu^+, for Fe^+, Co^+, and Ni^+ reactivity was observed with *n*-pentanenitrile; all three ions formed H_2, C_2H_4, and C_3H_6, albeit in completely different amounts [62,73]. As revealed by ^2H labeling of all four positions of the chain, dehydrogenation involved the $\omega/(\omega-1)$ positions, but preceding equilibria complicated the interpretation. Only by performing CID studies with all the isotopomeric dehydrogenation products of the individual ^2H-labeled nitriles, could the mechanism in Scheme 7 be formulated.

The complex of the γ/δ-unsaturated nitrile **14**, produced by remote functionalization, is in equilibrium with the hydrido-allyl complex **15** and CID upon the mixture afforded cleavage into HCN and butadiene, with both fragments observed. While for Co^+ the dehydrogenation proceeds directly, the encounter complex of Fe^+ with the pentanenitrile (**11**) is in equilibrium with the ferracyclobutane intermediate **18**. This ion, owing to its symmetry, equilibrates the α and γ positions of the substrate and leaves the β and δ positions unaffected. In contrast to the condensed phase, where numerous examples of isolated and well-characterized metallacyclobutanes are known (see, for example, ref. 79), in gas-phase organometallic chemistry a direct detection is still lacking, although they have been invoked frequently as reaction intermediates [1]. In fact, the available evidence for their formation is scarce and relies mainly on indirect information [80]. The viability of **18** may therefore give some useful hints which might reach far beyond gas-phase chemistry. For instance, the existence of positively charged ferracyclobutane intermediates in alkene cyclopropanations [81] with $[Cp(CO)_2Fe{=}CRR']^+$ has not been unambiguously confirmed or ruled out. They may or may not be involved, albeit *after* the transition state [81(g)], although recent results favor "backside closure" of the cyclopropane ring and hence would argue against them being involved [82]. Ferracyclobutanes have also been invoked in Fischer–Tropsch synthesis [83], and recently the preparation of the cyclic, perfluorinated complex $(CO)_4\overline{Fe(CF_2CF_2CF_2})$ could be accomplished [84]. Iron atoms also undergo photoinsertion into the C–C bond of cyclopropane to form ferracyclobutane itself [85], and a pentacyclic complex containing a ferracyclobutane ring has been prepared by insertion of thermally generated $Fe(CO)_4$ into the strained dibenzosemibulvalene [86]. The absence of cobaltacyclobutanes and nickelacyclobutanes in the pentanenitrile system could be interpreted as an inability of these ions to form the intermediates analogous to **18**. This assumption would be in line with other studies which showed that cobaltacyclobutane and nickelacyclobutane ions rearrange to more stable structures, while ferracyclobutane



Scheme 7. Dehydrogenation of *n*-pentanenitrile by Fe^+, Co^+, and Ni^+, including the different equilibria involved for the intermediates and the subsequent characterization of the products by CID.

ions were stable [80(a),(c)–(e),87]. It would then also indicate that the stability of these complexes is not only relatively independent upon substitution, but might even reflect inherent properties of these structures.

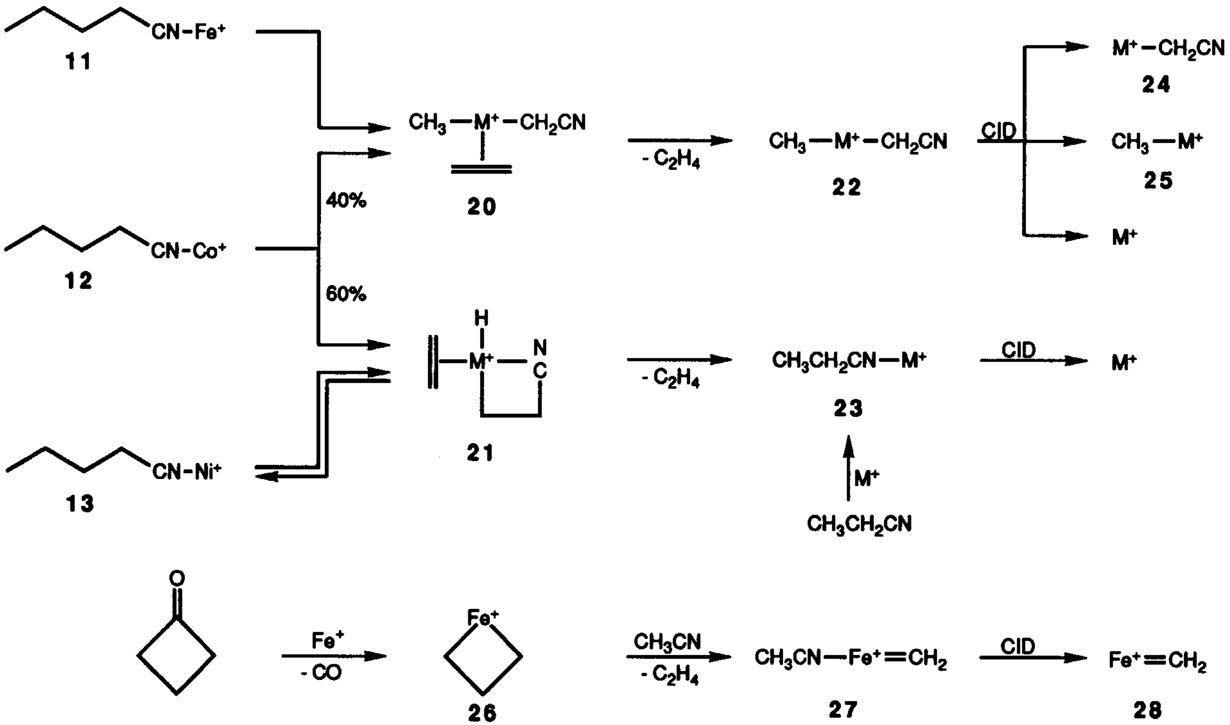
The Ni^+ complex **13** partially equilibrates the hydrogen atoms of the terminal C_2H_5 group via the hydrido-ethene complex **19**. For this intermediate it is now clearly impossible to maintain a linear end-on geometry of the $CNNi^+$ moiety; most likely slippage into a side-on coordination helps to release some of the strain involved.

Despite the fact that complicating equilibria were involved in the dehydrogenation of *n*-pentanenitrile, mechanistically the H_2 loss still proceeded by remote functionalization. Obviously, the alkyl chain is long enough so that the intermediates **6** and **7** can be formed without prohibitively large strain involved. For the alkene losses, the strain in the necessary intermediate **9** will be even larger, and it is therefore not too surprising that ethene is only partly formed by remote functionalization and formation of propene is due entirely to other mechanisms [62,73]. With the help of CID spectra that showed that isomeric $MC_3H_5N^+$ ions were formed upon loss of C_2H_4, the mechanism in Scheme 8 was derived.

While for Ni^+ ethene loss was exclusively due to remote functionalization and resulted in the formation of the propionitrile complex **23**, for Fe^+ all of the ethene originated from internal positions. Activation of the terminal C—C bond and subsequent *β*-C—C cleavage generates the intermediate **20**, which loses ethene to form complex **22**, an isomer of **23**. Upon CID, besides M^+, cleavage of the two metal—carbon bonds is observed. A third $FeC_3H_5N^+$ isomer was obtained upon reaction of the ferracyclobutane ion **26** with acetonitrile [81(a)]. CID upon the alkylidene complex **27** yielded loss of CH_3CN exclusively. The drastically different behavior of Fe^+ and Ni^+ is reflected in the intermediate Co^+ ion which reacted via *both* mechanisms to form a mixture of the isomeric $CoC_3H_5N^+$ complexes **22** and **23** [62]. The propene losses seemed to be mostly due to insertion into the C(α)—C(β) bond followed by *β*-hydrogen shift. Unfortunately, a straightforward interpretation was impossible due to scrambling processes involved. Reductive elimination of cyclopropane from **18** or analogous Co^+ or Ni^+ complexes could, however, be definitively excluded. In the condensed phase this is a common decomposition mode for metallacyclobutanes [81(a),88].

The only other metal ions that have been studied with primary nitriles are Mn^+ and Cr^+. With *n*-heptanenitrile, Cr^+ formed the adduct complex as sole product while for Mn^+ 20% dehydrogenation was also observed [67]. In the absence of collisional activation, which induced radical losses, Mn^+ (and Fe^+—Ni^+) ions were also unreactive with acetonitrile and propionitrile [53,89]. With several larger nitriles, Mn^+ was again found to be unable to react [68], and Cu^+ [77], Ag^+ [90], and Au [91] reacted with acetonitrile also only by formation of adduct complexes.

The predominance of the remote functionalization mechanism for linear nitriles reacting with Fe^+—Ni^+ contrasts markedly with the results obtained for tertiary nitriles. The first representative, 2,2-dimethyl propanenitrile (*t*-BuCN) afforded two



Scheme 8. Ethene loss from *n*-pentanenitrile by Fe^+, Co^+, and Ni^+ with concomitant formation of isomeric $MC_3H_5N^+$ isomers and characterization of these, as well as a third, formed by decarbonylation of cyclobutanone and subsequent reaction with acetonitrile, by CID.

completely "new" products in the reaction with Fe^+ [40]. These are a complex of Fe^+ with [H,C,N], formed by loss of C_4H_8, and $Fe(C_4H_8)^+$ by loss of [H,CN]; both obviously arise from a common intermediate with a $Fe(C_4H_8)(H,CN)^+$ structure. The similarity to the products generated from main-group ions and alkyl halides or alcohols is also evident. As will be discussed later, transition-metal ions do form the same products with these substrates, but for them a different mechanism was initially proposed by Allison and Ridge, who claimed a fundamental difference between main-group and transition-metal ions [38,92]. It was assumed that transition-metal ions insert into the bond to the functional group of the substrate, undergo β-hydrogen shift and rearrange by transfer of the hydrogen to the functional group so that a di-ligated intermediate is formed which competitively loses one of its ligands.

For the *t*-BuCN system, however, this mechanism can be discarded by comparison with the reactions of 2-isocyano-2-methyl propane (*t*-BuNC), which also afforded $Fe(H,C,N)^+$ and loss of (H,CN) upon reaction with Fe^+. If the insertion/β-H shift mechanism were active, one would expect complexes **33** to be formed, i.e. $M(HNC)^+$ from *t*-BuCN and $M(HCN)^+$ from *t*-BuNC (Scheme 9). High-energy CID could distinguish the $Fe(H,CN)^+$ ions formed from *t*-BuCN and *t*-BuNC, and it turned out that in fact **37** was the product, respectively, i.e. $M(HCN)^+$ from the nitrile and $M(HNC)^+$ from the isonitrile [40,70]. To explain this result, an ion/dipole mechanism was invoked [8(c),(d),28,41]. Complexation of M^+ to the functional group XY induces cleavage of the C—XY bond and generates the ion/dipole complex **35***. Simple separation of the two constituents is, however, often precluded by the fact that this would be endothermic. The complex therefore rearranges by protonation of the XYM dipole** by the incipient carbenium ion; since Y is "blocked" by the complexation to M, this step involves the "free" atom X and generates the di-ligated complex **36** which eventually dissociates to **34** and **37**.

The branching ratio between the two products has to reflect the relative binding energies of the two ligands in **36**. This can indeed be seen from another comparison between *t*-BuCN and *t*-BuNC [40]. If **36** is formed from *t*-BuCN, it contains an HCN molecule, and experimentally it was found that the complex preferentially loses this ligand and retains the isobutene. Quite contrary, **36** produced from *t*-BuNC, and therefore containing HNC, preferentially retained this ligand and lost C_4H_8. This behavior is exactly what would be expected from the relative binding energies of nitriles versus isonitriles as it can be shown that the latter are stronger bound [40,54(b)].

Further evidence for the ion/dipole mechanism was provided by the reactions of Co^+, Ni^+, and Cu^+ with 2-methyl butanenitrile or 2-ethyl butanenitrile and of

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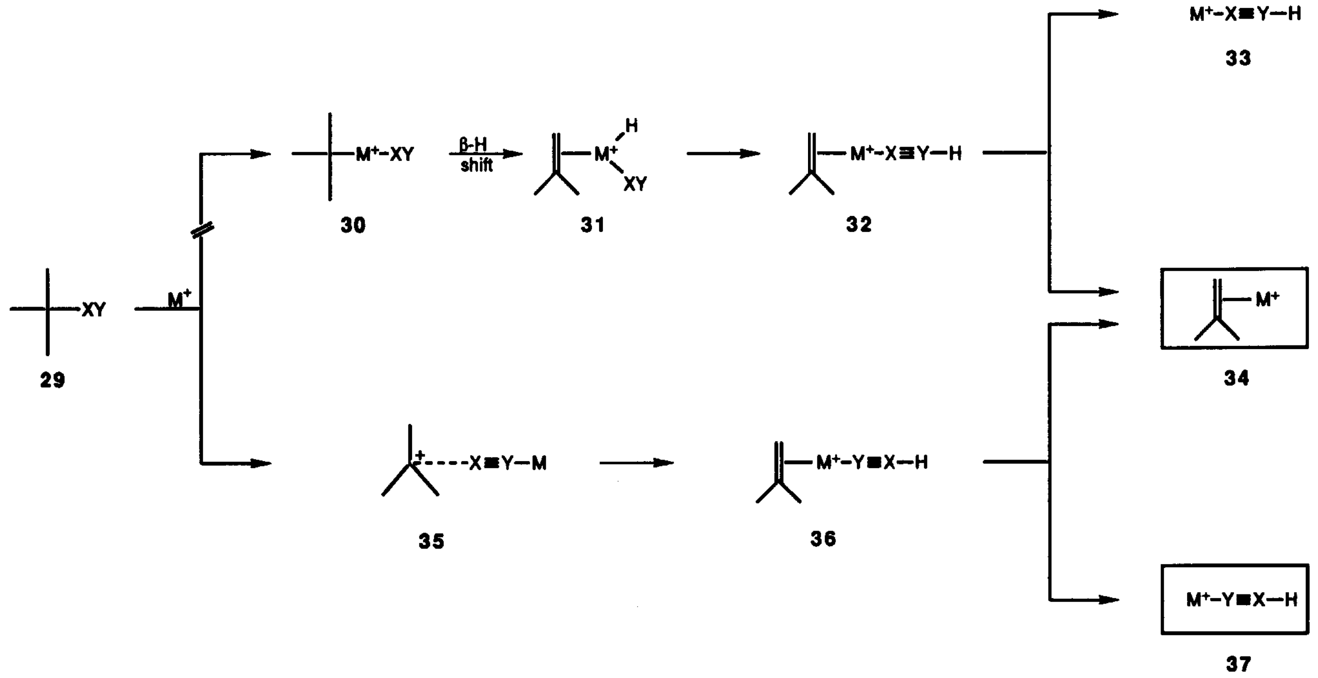
* There is considerable precedent for ion/(induced) dipole complexes as intermediates in unimolecular reactions of gaseous cations. For reviews, see ref. 93.

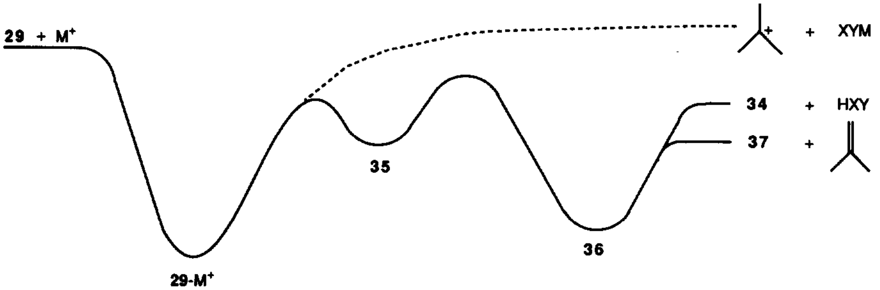
** For theoretical studies on MCN and MNC, see ref. 94 (a)–(d). Heterolytic cleavage of *t*-BuNC has also been discussed for the reaction with $Ru(dmpe)_2$, which eventually gives rise to $Ru(dmpe)_2(H)(CN)$ [94(e)].



Scheme 9. Schematic representation of the ion/dipole mechanism, exemplified for the reactions of *t*-BuCN and *t*-BuNC with transition-metal ions M^+

Fe^+ with 2,2-dimethyl butanenitrile [28,41,95]. In all these systems, $M(HCN)^+$ ions (with proven structure) as well as loss of HCN were observed. Ion/dipole complexes are known to be quite long-lived [93,96], being trapped on the reaction coordinate by a potential-energy barrier on one side and an entropic bottleneck on the other; on the contrary, hydrogen rearrangements in carbenium ions are fast processes [97]. It can therefore be expected that occasional H/D scrambling in **35** should be detectable. And indeed, for the above-mentioned systems, ^2H labeling proved that not only the β-hydrogen atoms, but in fact all positions contributed to the hydrogen-transfer step [28,41].

A very general energy diagram for the mechanism in Scheme 9 is provided in Scheme 10. Without putting any emphasis to the depth of the basins, it is meant to demonstrate the presence of different minima along the reaction coordinate. For simplicity it also ignores any centrifugal barriers at the entrance and the exits. The relative energetic order of **37** and **34** would match the case of *t*-BuNC forming $M(HNC)^+$ and HNC; for *t*-BuCN they would have to be reversed. Quite similarly, for many metal ions the $C_4H_9^+$ product would have to be energetically lower than the separated **29** and M^+.



Scheme 10. Energy profile for the ion/dipole mechanism in Scheme 9.

Some of the observations just listed could still be explained with an insertion/β-H shift mechanism if further assumptions are invoked. For instance, the formation of **36** in lieu of **32** could be explained by a reductive elimination of H–XY from **31** where the HXY molecule does not depart from the complex but swings around to coordinate through Y to the metal ion. It is not obvious, however, why this should happen; after all, this would be contrary to the postulated initial insertion **29**→**30** where it seemed to be favorable for the metal ion to form an M–XY bond. By going from **31** to **36** it would lose this bond again. In addition, one would have to exclude direct alkene loss from **31**, as for the $M(H,CN)^+$ product $H{-}M^+{-}(XY)$ structures could be excluded. The scrambling of the hydrogen atoms could still be explained with reversible β-hydrogen shifts that lead to isomeric alkene complexes via different alkyl-hydride structures, but the last finding to be presented at this point certainly cannot be refuted by invoking the insertion/β-H shift alternative.

In the 2-methyl butanenitrile and 2-ethyl butanenitrile systems there are three different mechanisms active with Fe^+–Cu^+ (see below), and one of them, as already mentioned, is the ion/dipole mechanism that leads to the formation of HCN and $M(HCN)^+$ ions. The relative contribution of this mechanism, as compared with the other two, steadily increases along the row from Fe^+, where it is absent, to Cu^+, where it is the sole mechanism operative. As already outlined above, Cu^+ is unlikely to insert into any bonds due to its very stable d^{10} ground state. It is, however, still able to react as a Lewis acid and can hence still react by the ion/dipole mechanism which is devoid of any insertion steps. The other two mechanisms operative for the secondary nitrile include insertion steps and are therefore inaccessible to Cu^+, but not to Fe^+–Ni^+. Insertions are also impossible for the main-group ions discussed in the previous section, in contrast to all of the steps in the ion/dipole mechanism. It is therefore proposed that the wavy arrow in Scheme 4 can actually be replaced with a sequence along the lines of Scheme 9 and that Scheme 10 probably describes the energetic situation better than Scheme 5.

An important conclusion that can be derived from this result is that *the extent by which the ion/dipole mechanism is operative depends on the need for it.* This postulate gains additional credence from studies employing isonitriles. The different behavior of *t*-BuNC and *t*-BuCN already indicates that a metal-ion-induced isomerization of the isonitriles* to the thermodynamically more stable nitriles [99] is absent, although this long-known reaction [100] occurs in solution [101], at metal surfaces [102], or in the gas phase at elevated temperatures [103]. A distinctly different behavior than with nitriles has also been observed in the reactions of Fe^+ with several *n*-alkyl isocyanides [104]. For short chain isocyanides, where remote functionalization is not yet possible, formation of $Fe(HNC)^+$ by the ion/dipole mechanism was operative. ^2H labeling showed that the origin of the hydrogen was unspecific, thus the intermediate carbenium ions have enough time to rearrange by hydride shifts. With increasing chain length, the remote functionalization begins to compete, and for isonitriles it is mainly H_2 that is formed, although ethene was also present. In contrast to the ion/dipole mechanism, the dehydrogenation was specific and involved the $\omega/(\omega-1)$ positions as expected. Cu^+ has also been studied with $C_nH_{2n+1}NC$ ($n=2$–9) and some ^2H- and ^{13}C-labeled isotopomers thereof [105]. Here, the products of the ion/dipole mechanism, $Cu(HNC)^+$ [105] and HNC, dominated the CID spectra of the $Cu(RNC)^+$ complexes in all cases. Additional signals, that were observed even in metastable-ion spectra, included carbenium ions R^+ by loss of CuCN. Obviously the difference between the R–NC and the Cu–CN bond energies is sufficiently large to drive the separation of the ion/dipole intermediates **35**. In the CID spectra, similar radical losses as for the $Cu(RCN)^+$ complexes were present, viz. CH_2NC–Cu^+ and CH_2CH_2NC–Cu^+ by simple C–C cleavage during the collision process and (CH_2=CH–NC)Cu^+ by consecutive loss of two radicals.

In order to get an overview of the d block, nearly all transition-metal ions were

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* For reviews on metal-isocyanide complexes, see ref. 98.

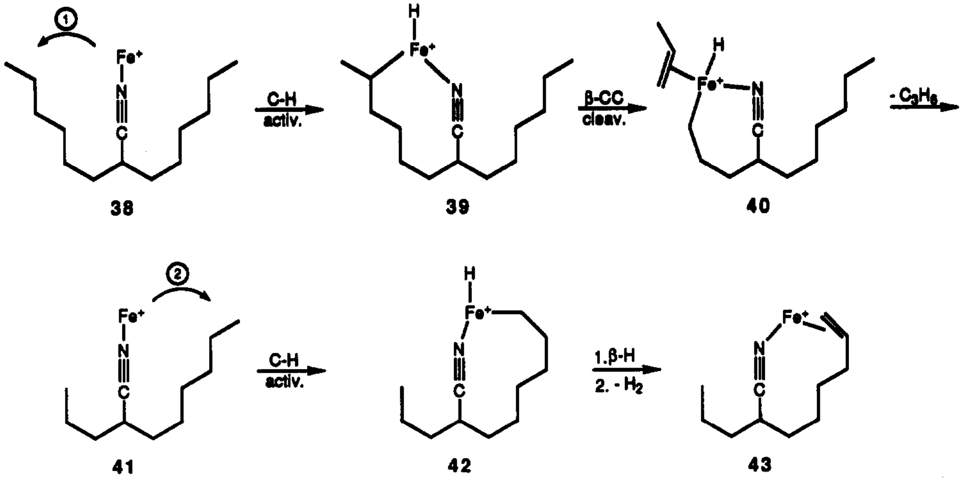
reacted with *n*-propyl, *n*-butyl, and *n*-pentyl isocyanide [105]. Interestingly, the observed reactivity reflected the behavior that the individual ions had revealed earlier with various other substrates [1], so that it can be regarded as being due to the ions' intrinsic properties. Dehydrogenation, or C—H activation, was very prominent for early transition-metal ions such as Ti^+ and V^+ and nearly all second- and third-row ions, except for groups 11 and 12, where there are filled d shells. Fe^+ in the first row was also seen to dehydrogenate the isonitriles, as discussed above, but the tendency for C—H activation rapidly decreases for Co^+ and Ni^+. The ion/dipole mechanism was operative for all transition-metal ions, but was reduced in importance for those ions that efficiently dehydrogenated the substrates. On the contrary, it was most dominant for groups 6 and 11, i.e. those ions that are often unable to afford C—H or C—C activations. As the ion/dipole mechanism avoids insertion steps, it may be the only alternative left for these ions.

Ligand-detachment signals were found to be a good indicator for lacking reactivity as they were most pronounced in cases where no other reactions were possible. For instance, short substrates were always more prone to loss of the intact ligand than larger substrates where alternative pathways are accessible. Maximum amounts of ligand detachment were found for Mn^+, a metal ion that rarely gives rise to cleavage products of whatever kind. Additional support for this hypothesis comes from a study dealing with the various mechanisms operative for Fe^+ and secondary nitriles. Ligand detachment is only observed in cases where other mechanisms are either completely impossible like in the case of $(CH_3)_2CHCN$ or energetically unfavorable due to highly strained intermediates. As soon as the other alternatives become available, the ligand-detachment signals rapidly diminish [41].

Secondary nitriles turned out to be very interesting as they not only provided a transition between the remote functionalization and the ion/dipole mechanism but also led to the discovery of a third process that commenced with an insertion into the C—CN bond. Initial work was concerned with symmetric, long-chain nitriles of the type R_2CHCN in order to get a handle on the kinetics of the remote functionalization mechanism. Metastable-ion spectra of 2-butyl hexanenitrile ($(n\text{-}C_4H_9)_2CHCN$) and a rather extensive set of eight ^2H-labeled isotopomers showed that 97% of the products were formed by remote functionalization, namely hydrogen and ethene [41,74,107]. They both originated from the $\omega/(\omega-1)$ positions of the chains, and comparison of the labeling data allowed to deduce intramolecular kinetic isotope effects (KIEs) for the individual steps in Scheme 6. While the initial oxidative addition is not rate-determining, for the ethene loss it is the final detachment step that shows a secondary KIE, and for the dehydrogenation both the β-H shift and the reductive elimination are associated with a primary KIE.

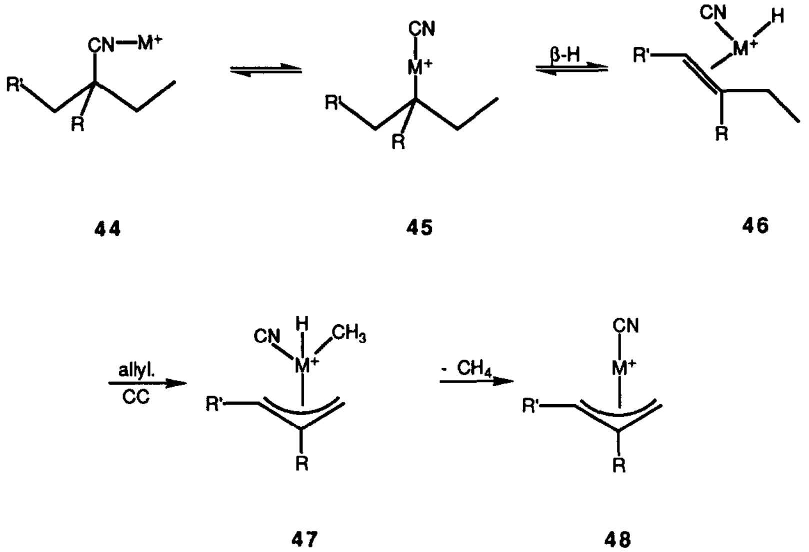
A distinct feature in MI spectra of the secondary nitriles are abundant CH_4 losses for small compounds and other C_nH_{2n+2} losses for nitriles with two long chains. Since the methane loss may be observed with some tertiary nitriles as well, it will be discussed later. As was already briefly mentioned above, loss of $[C_nH_{2n+2}]$

was observed for primary nitriles, too, but only upon collisional activation and as a result of a consecutive reaction in which loss of H_2 was followed by loss of alkenes [66]. The question, if loss of $[C_nH_{2n+2}]$ in the case of secondary nitriles also corresponded to eliminations of H_2/C_nH_{2n} or rather to intact alkanes, was solved using MS/MS and ^{2}H-labeling techniques [41,64]. The MS/MS experiments showed that loss of C_2H_6 or C_3H_8 from RR'CHCN was actually due to loss of C_nH_{2n}/H_2, but unlike the linear nitriles, loss of the alkene *preceded* dehydrogenation and not vice versa. Even more interesting was the observation of exclusively $[C_2H_3D_3]$ and $[C_3H_4D_4]$ losses from $(CD_3(CH_2)_5)_2CHCN$, a result which could only be rationalized by a *successive double remote functionalization of both alkyl chains* (Scheme 11). The driving force and most likely explanation for the absence of the reversed sequence, i.e. loss of H_2/C_nH_{2n}, is the formation of the chelated complex **43**. Dehydrogenation of the secondary nitriles already produces bidentate complexes while alkene losses generate shortened ligands with still only one coordination site. Other known examples for double remote functionalization in the gas phase are ketones [63,64] and imines [108]; in the condensed phase, an example for a rigid molecule has been reported only recently [109].



Scheme 11. Double remote functionalization of secondary nitriles, exemplified for the "C_3H_8" loss from 2-hexyl octanenitrile; initial alkene loss from one chain is followed by dehydrogenation of the other chain.

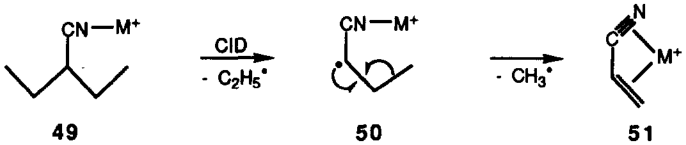
Most unusual is the methane loss that was observed for secondary nitriles and also $C_2H_5C(CH_3)_2CN$ reacting with Fe^+ and, albeit less intense in that case, Co^+. As expected, three of the hydrogens originated from the chain termini but the fourth was not provided by the $(\omega-2)$ position but exclusively from a position *β to the cyanide group*. The reasons for this finding are not particularly well understood. Although the process was not very intense for long chain nitriles, for example 3% for the above-mentioned $(n\text{-Bu})_2CHCN$ [41,74], the driving force remains unclear. It was, however, somewhat more obvious for small substrate molecules where it may be produced in amounts up to 58% for Fe^+ and 2-ethyl butanenitrile [27,28,41,95]. As depicted in Scheme 12, the reaction commences with an insertion of the metal ion into the C—CN bond followed by a β-hydrogen shift. Reductive elimination of HCN from the resulting intermediate **46** must be kinetically hindered, though, since it is not observed. Instead, a terminal C—CH_3 bond is activated in the following, and methane is reductively eliminated. In cases where the methane loss reaches significant values, the C—CH_3 bond is simultaneously in an allylic position to the newly generated double bond. This facilitates its cleavage and favors the CH_4 loss over other processes such as remote functionalization or the ion/dipole mechanism. As soon as one chain was, however, long enough to permit the operation of the former, it became dominant.



Scheme 12. Methane loss from small branched nitriles by initial C—CN insertion of the metal ions (M^+ = Fe^+, Co^+) followed by β-H shift, allylic C—C insertion, and reductive elimination.

Transitions from one mechanism to another are also very obvious from comparisons of different metal ions. The reactions of 2-methyl butanenitrile [28] and 2-ethyl butanenitrile [95] with all first d-row metal ions from Ti^+ through Zn^+ have been studied employing sector and FTICR instruments as well as ^2H labeling. The chemistry of Fe^+ has already been described and proceeds according to Schemes 6 and 12. Additional features included a degenerate isomerization for the smaller substrate in the course of the methane loss, weak losses of $CH_3\cdot$ radicals from intermediate **47**, and scrambling of the "ethyl" hydrogens in both substrates due to an equilibrium between [Fe]—C_2H_5 and [Fe](C_2H_4)—H structures. This latter finding was also observed for butanenitrile and 2,2-dimethyl butanenitrile [41]. A strikingly different behavior was encountered for Cu^+, which reacted exclusively by the ion/dipole mechanism due to restrictions imposed by its d^{10} configuration and as discussed above. For the intermediate Co^+ and Ni^+ ions, varying contributions from the three mechanisms were observed with Co^+ reacting by all three of them and Ni^+ by the remote functionalization and the ion/dipole mechanism. Altogether, a gradual switching from one mechanism to the other was obvious from the comparison of Fe^+ to Cu^+ and showed the limitations for the individual ions. Fe^+ is unable to react with secondary nitriles by the ion/dipole mechanism but induces roughly equal amounts of remote functionalization and methane loss by allylic insertion. Co^+ is able to react via all three mechanisms but strongly prefers the remote functionalization; Ni^+ does not react via initial C—CN insertion but reveals, compared to Co^+, an increased amount of products from the ion/dipole mechanism but with remote functionalization still being favored. Cu^+ may only react via intermediate ion/dipole complexes. This comparison also shed a new light on the reaction of Co^+ with the lower homologue 2-methyl propanenitrile ($(CH_3)_2CHCN$) that yielded $Co(HCN)^+$ and $Co(C_3H_6)^+$ by loss of HCN [67]. This has been explained by invoking an insertion/β-hydrogen shift mechanism, but as Scheme 12 shows, reductive elimination of HCN does not occur, even though Co^+ is able to insert into the C—CN bond. Both products can therefore only be due to the operation of the ion/dipole mechanism.

The early transition-metal ions Ti^+ and V^+ reacted with both 2-methyl and 2-ethyl butanenitrile predominantly by C—H activation, with either dehydrogenations or dehydrogenations combined with the loss of other small neutral molecules prevailing [28,95]. The reaction mechanisms were difficult to derive, though, as the occurrence of multiple losses per se complicated the interpretation of the labeling data, and there also were reversible steps involved that worsened the case even further. Ti^+, more extensively than V^+, gave rise to multiple dehydrogenations with a much higher percentage of $2H_2$ and even $3H_3$ losses, for instance. Cr^+, Mn^+, and Zn^+ were unreactive with the two secondary nitriles; under FTICR conditions, adduct formation was observed and exclusively ligand detachment in MI spectra. CID upon the chromium, manganese, and zinc adduct complexes further underlined the unreactive nature of these ions. In contrast to adduct complexes of "reactive" metal ions, where similar products as in ion/molecule reactions were observed [1,27–32,74], radical losses prevailed, and there was no indication for an active involvement of the metal ions. Ligand detachment always led to the most abundant signal in the low-energy CID spectra; besides, low-intense products from the ion/dipole mechanism were seen together with the specific formation of acrylonitrile complexes in the case of 2-ethyl butanenitrile. The latter are formed by a sequence of two radical losses as depicted in Scheme 13. Simple C—C cleavage in the course of the collision process generates the radical ion **50** and is supported by delocalization of the unpaired electron to the CNM^+ moiety. It subsequently loses a methyl radical, a process fueled by the formation of the bidentate acrylonitrile ligand. The formation of $CuC_3H_3N^+$ ions from linear nitrile and isonitrile complexes of Cu^+ upon high-energy CID was rationalized by the same mechanism (see above).



Scheme 13. Collision-induced formation of acrylonitrile complexes from adduct complexes of Cr^+, Mn^+, and Zn^+ with 2-ethyl butanenitrile.

Similar to Cu^+ [106], Cr^+ has been found to react with *t*-BuCN [8(c),(d)] and *t*-PentCN [110] according to the ion/dipole mechanism and affording $Cr(HCN)^+$ and loss of HCN. Like Cu^+, Cr^+ with a half-filled d^5 shell and Mn^+ and Zn^+ with ground state d^5s^1 or $d^{10}s^1$ configurations are unlikely to undergo oxidative additions, and it is therefore not surprising that, if they react at all, they do so by means of the ion/dipole mechanism where no insertion steps are incorporated.

(ii) Isocyanates and isothiocyanates

Isocyanates have found interest as model substrates for gas-phase reactions as there was already some information available about their behavior with a heterogeneous catalyst. While uncatalyzed pyrolysis of isopropyl and *tert*-butyl isocyanate afforded the alkenes and isocyanic acid (HNCO) only at temperatures above 900 K (reaction (12)), Ni_x clusters on a carbon support (Ni_x/C_∞) significantly altered the ongoing chemistry [111].

$$C_nH_{2n+1}NCO \rightarrow C_nH_{2n} + HNCO \qquad (12)$$

At 500 K, Ni_x/C_∞ is able to catalyze the decomposition of isopropyl isocyanate to afford carbon monoxide, methane, and acetonitrile

$$(CH_3)_2CHNCO \rightarrow CO + CH_4 + CH_3CN \qquad (13)$$

Since CO was formed already at 400 K, the assumption of an intermediate, surface-bound nitrene seems justified; at 500 K this nitrene yields CH_4 and acetonitrile, which desorbs from the surface at a still slightly higher temperature. An analogous reaction for *t*-BuNCO was not observed, but Ni_x/C_∞ catalyzed isobutene/HNCO formation at temperatures as low as 500 K [111].

The differences between i-PrNCO and *t*-BuNCO are as unclear as is the underlying reason for the change from reaction (12) to reaction (13). To investigate that, different metal ions were studied with several isocyanates to find the gas-phase analogue of reaction (13) [112–114]. The metal ions studied (Ti^+–Zn^+) could be arranged in two groups, early (Ti^+, V^+) and late (Cr^+–Zn^+) transition-metal ions. The latter showed a behavior that was related to the pyrolysis while the former reacted analogously to (13).

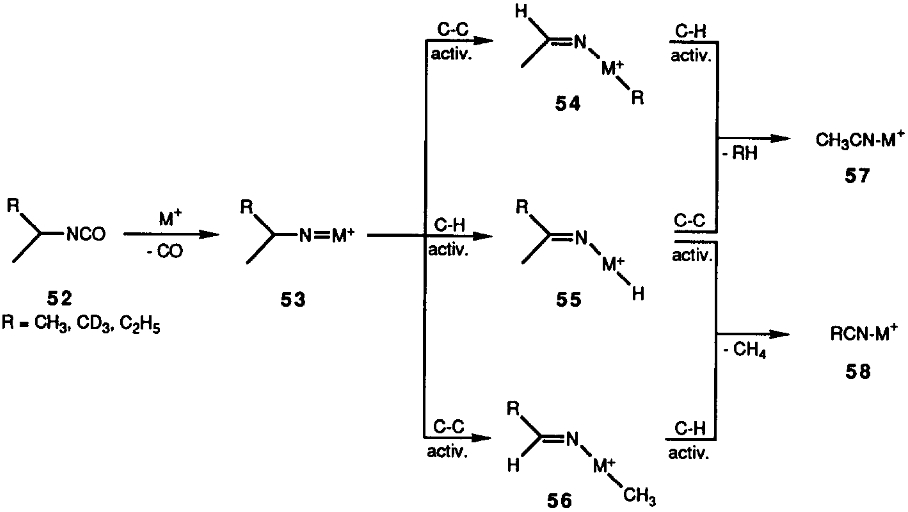
All of the late transition-metal ions reacted with i-PrNCO to afford

$M(HNCO)^+$ and $M(C_3H_6)^+$ by loss of HNCO, in a similar ratio and with similar kinetic isotope effects involved (around 1.5, respectively). The KIEs were determined from $CD_3(CH_3)CHNCO$, as $(CH_3)_2CDNCO$ had shown that only the methyl groups provided the hydrogen for $M(HNCO)^+$ and HNCO. *sec*-Butyl, *tert*-butyl, and *tert*-pentyl isocyanate revealed an analogous behavior with Cr^+–Zn^+. Again, $M(HNCO)^+$ and $M(alkene)^+$ ions were formed, but also $C_nH_{2n+1}^+$ by loss of [MNCO], and part of the $M(alkene)^+$ ions decomposed further by loss of H_2, CH_4, or C_2H_4 [112–114].

To explain the formation of these products, two pathways may be considered; the insertion/β-hydrogen shift as well as the ion/dipole mechanism could account for them (cf. Scheme 9). Although the structure of the $M(HNCO)^+$ ions could not be determined, there is good reason to believe that in fact the ion/dipole mechanism is responsible for all of the observed products. First of all, the very similar behavior of all late metal ions, including those for which oxidative additions are very unlikely for electronic reasons (Cr^+, Mn^+, Cu^+, Zn^+), shows that the same mechanism is operative. Not only were similar product distributions observed (except for subsequent decompositions in the case of Fe^+–Ni^+), the results for ^2H-labeled isotopomers also showed similar labeling distributions. It is hardly conceivable that two different mechanisms would proceed with the same ease *and* outcome, and as for some ions insertions are impossible, it can only be concluded that for all ions the ion/dipole mechanism applies.

The labeled isocyanates had all shown that only β-hydrogen atoms contributed to the proton-transfer step and showed up in the $M(HNCO)^+$ and HNCO products. This seemingly contradicts the idea that the ion/dipole mechanism is active, which could be expected to reveal H/D scrambling in the incipient carbenium ions in the $[C_nH_{2n+1}^+ \cdots NCOM]^*$ intermediates. At this point it is necessary to go back to the characteristics of ion/dipole mediated gas-phase reactions. The "entropic well" in which ion/dipole intermediates reside is flanked by a tight and a loose transition state. The tight TS precedes ion/dipole complex formation while the loose TS is reached subsequently. The loose TS is rate-controlling at low energies while at higher energies, passage through it becomes so rapid that the tight TS becomes rate-determining [93]. In that case it is predicted that other reactions with transition states at energies between those of the tight and loose TS, such as H/D scrambling, will also rapidly diminish in importance. In other words, if the reactions of Cr^+–Zn^+ with secondary and tertiary isocyanates sufficient energy is available, no H/D scrambling, and hence contributions from positions other than β, would be expected. A criterion for this assumption is the observation of carbenium ions by NCO abstraction. Competition between simple dissociation and proton transfer is a function of the amount of energy contained in the ion/dipole complex. Proton transfer will be prevented when the initial fragments separate too rapidly for the partners to rotate into a configuration permitting the transfer. The simultaneous appearance of carbenium ions and absence of H/D scrambling is therefore fully in line with the expectations for the ion/dipole mechanism and supports its proposed operation. For ion/dipole complexes containing 2-propyl cations, it is already well known that isomerizations to 1-propyl cations are only observed if sufficient energy is available, otherwise no H/D scrambling can be noted (see, for example, ref. 115).

With Ti^+ and V^+ a different situation arose in the reactions of the isocyanates [112–114]. Secondary isocyanates were distinct from tertiary isocyanates in that products due to the ion/dipole mechanism, albeit present, were only of minor importance. Instead, nitrile-complex formation was observed. While i-PrNCO with both Ti^+ and V^+ yielded $CH_3CN{-}M^+$ by loss of CO/CH_4, *sec*-BuNCO in addition to $CH_3CH_2CN{-}M^+$ by loss of CO/CH_4 also formed $CH_3CN{-}M^+$ by loss of CO/C_2H_6. The mechanism in Scheme 14 accounts for those findings and is supported by the following arguments.



Scheme 14. Formation of nitrile complexes from secondary isocyanates by the early transition-metal ions Ti^+ and V^+.

Nitrenes such as **53** are common intermediates in the condensed-phase chemistry of isocyanates reacting with transition-metal complexes [116–119]* and in the surface-catalyzed process [111], and it is hence very likely that decarbonylation is also the first step en route to the nitrile complexes. Labeling further proved the formal presence of a 1,1-elimination for both secondary nitriles. Which of the two necessary activation steps actually precedes the other, C—H or C—C activation, could not be elucidated.

With the two tertiary isocyanates *t*-BuNCO and *t*-PentNCO no nitriles were formed upon reaction with Ti^+ or V^+. In addition to a plethora of small products, the majority of the losses were those of the ion/dipole mechanism [114]. Obviously,

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* For a review on transition-metal complexes containing nitrene ligands, see ref. 119.

two C—C activations are impossible in Scheme 14 and therefore nitrile formation is suppressed in favor of other processes. This was the same behavior as found for the Ni_x/C_{∞}-catalyzed reactions [111].

For the differences between Ti^+ and V^+ on the one hand and Cr^+–Zn^+ on the other, the metal ion's binding energies to nitrenes were held responsible [112–114]. The early transition-metal ions form very strong bonds with the simplest nitrene, namely $D^0(HN{=}Ti^+) = (111 \pm 3)$ kcal mol^{-1} [120] and $D^0(HN{=}V^+) = (99 \pm 4)$ kcal mol^{-1} [121]. This is opposed to Fe^+, which has been found to possess a much weaker binding energy of $D^0(HN{=}Fe^+) = (54 \pm 14)$ kcal mol^{-1} [122]. Cr^+–Cu^+ were also unreactive with ammonia [16,76,122,123], while Sc^+–V^+ were able to dehydrogenate NH_3 exothermically to form $HN{=}M^+$ nitrene complexes [120–122,124].* In the absence of any barriers, this was tentatively interpreted as $D^0(HN{=}M^+) < 96$ kcal mol^{-1} for M = Cr–Cu. The conclusion that in the gas phase the nitrene binding energy was the pivotal point for the nitrile formation was also transcribed in the condensed phase, and it was proposed that catalysts with high binding energies for surface nitrenes should work best for the formation of nitrile complexes from isocyanates [112–114]. This gained some support from adsorption studies of CH_3NCO on single-crystal surfaces which showed that dissociation into CH_3N and CO was only observed when it was exothermic [125].

In the course of the studies on isocyanates, an interesting observation was made for the secondary reactions of Cr^+–Zn^+ [114,126]. While for $M^+ = Cr^+$, Mn^+, and Zn^+, the primary $M(HNCO)^+$ and $M(alkene)^+$ products reacted with the secondary isocyanates to form $M(RNCO)^+$ adduct complexes by simple ligand exchange, for Fe^+–Cu^+, isomeric $M(HNCO)(alkene)^+$ ions were obtained. In the case of tertiary isocyanates, Cr^+ behaved like Fe^+–Cu^+, and only Mn^+ and Zn^+ reacted by simple ligand exchange. As shown in Sect. B, in sector studies, adduct complexes are selected out of a CI plasma in which they are formed by a sequence of ion/molecule reactions. The preceding observations, although obtained under FTICR conditions, show, however, that ligand exchange can go along with dissociation and may lead to unexpected isomerizations.

Some isothiocyanates have also been studied [127,128]. Using a complete set of ^2H-labeled isotopomers, the reactions of Ti^+–Zn^+ with butyl isothiocyanate were studied under FTICR conditions [128] and compared with those of Fe^+ with RNCS ($R = C_2H_5, C_3H_7, C_4H_9$) in metastable-ion decompositions [127]. Under FTICR conditions, the main product for most of the metal ions was $MHNCS^+$ formed by the ion/dipole mechanism. For Ti^+ a significant amount of sulfur abstraction was also observed, and for Cr^+ the losses of H_2 and H_2S were very prominent too. While the dehydrogenation was unspecific, for the H_2S loss the major hydrogen contributions came from C(1) and C(4) and less so from C(2) and C(3). Unlike the Fe^+ case described below, the mechanism for this dehydrosulfurization could thus not be

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* $D^0(HN{=}Sc^+)$ has been studied theoretically in ref. 7(b). See also ref. 124(a).

determined. Mn^+ was the only ion that did not form $MHNCS^+$ at all, but produced mainly alkenes, C_2H_4 and C_3H_6. Ethene accounted for 57% of the products and was formed exclusively from the α- and β-CH_2 groups. Insertion into the C(1)–NCS bond followed by β-C–C cleavage was proposed to explain this finding [128]. Propene was formed classically by insertion into the C(1)–C(2) bond followed by β-hydrogen shift. Fe^+, Co^+, and Ni^+ reacted very similarly and yielded almost exclusively the products from the ion/dipole mechanism, i.e. $MHNCS^+$, NHCS, $HNCS/H_2$, and $C_4H_9^+$ by loss of [MNCS]. H/D scrambling was noted and involved all positions of the substrate. As the NCS abstraction was of minor importance (3% for Fe^+ and 2% for Co^+), this was in line with the expectations on the mechanism discussed above.

The reaction of Fe^+ with *n*-BuNCS represents one of the rare cases where large differences between FTICR and MI results were observed. Although the same products were formed, the intensities differed greatly. The products from the ion/dipole mechanism were also observed in the MI spectra but the main product (35%) in this case was loss of H_2S, which occurred in the FTICR spectra only with a meager 2% abundance. The H_2S loss was of negligible importance for ethyl and propyl isothiocyanate reacting with Fe^+ under MI conditions. There again, $FeHNCS^+$ and loss of HNCS were the major products. As seen from the labeled butyl isothiocyanates, the hydrogen atoms for the H_2S were mainly provided by the $\omega/(\omega-1)$ positions of the chain. The mechanism in Scheme 15 has been proposed to account for this finding. Sulfur abstraction yields a complex of FeS^+ with butyl isocyanide (**60**); this process has been noted for Fe^+ before [129] and is also known in solution for isothiocyanates [118(f),(i),130] as well as other substrates [118(i),131]* with a good leaving group. The following steps are analogous to the remote functionalization mechanism in Scheme 6, only that a ligated metal ion is involved. It has been shown that FeO^+ is also able to react by remote functionalization [132]. In solution, it has been found that HS^- attack at coordinated isocyanides may give rise to isothiocyanate complexes [133], which would represent the reverse reaction from **62** to **59**. The overall process in Scheme 15 constitutes an intramolecular variant of the industrially important hydrodesulfurization (HDS) [134].

Further products that were more abundant in the MI spectra were loss of H_2 and C_2H_4 which were formed by remote functionalization. The suppression of the remote functionalization products in favor of the ion/dipole products in the FTICR spectra might be taken as an indication that MI spectra are sampling slightly "cooler" products. This contention is based on the finding that the ion/dipole mechanism applies only in cases where no other reactions are accessible. The drastic shift for Fe^+/*n*-BuNCS showed that this system represented a borderline case where small differences in energy greatly influenced the mechanisms. A recent comparison of the reaction of Cu^+ with octynes also showed decreased abundances of remote function-

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* For a theoretical study, see ref. 131(m).

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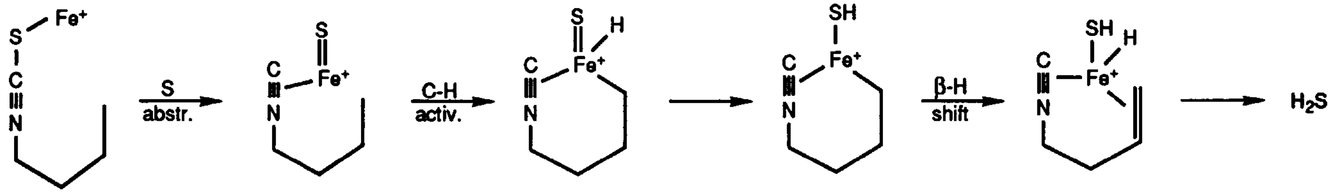


59 **60** **61** **62** **63**

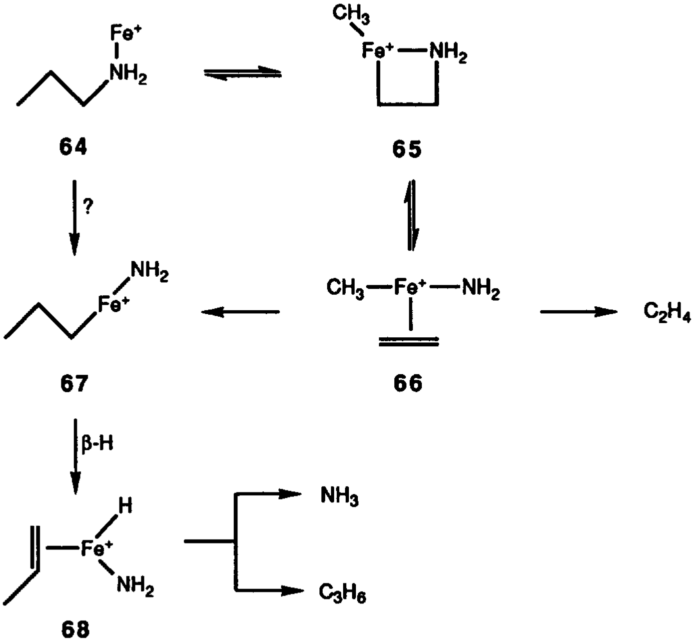
Scheme 15. Dehydrosulfurization of butyl isothiocyanate by Fe^+ via initial sulfur abstraction and subsequent remote functionalization of the alkyl chain.

alization products in FTICR experiments as compared to MI spectra; remote functionalization was also found to be a low-energy process [135]. Cu^+ with butyl isothiocyanate afforded exclusively $MHNCS^+$ and loss of NHCS, while Zn^+ besides these two products reacted predominantly by charge transfer to $C_4H_9NCS^{+\cdot}$ and its decomposition products [128]. This finding was in line with the ionization potentials of Zn (9.394 eV [136]) and *n*-BuNCS (9.02 eV [137]). The similarity between most of the first-row metal ions, including for instance Cu^+, again excludes the operation of the insertion/β-hydrogen shift mechanism.

(iii) Primary amines

Already the simplest primary amine, methylamine, was observed to react with bare metal ions. Dehydrogenation was noted for Fe^+ [138], Ru^+ [138], and Rh^+ [138], while Co^+ [138,139] and Ni^+ [138] afforded a mixture of H_2 loss and the product of a hydride abstraction, $CH_2{=}NH_2^+$. CuH is also the sole product generated with Cu^+ [140]; in contrast, Ag^+ formed adduct complexes only [140]. An adduct complex is also the only product of the reaction of Al^+ with ethylamine [141]. With the early transition-metal ions Ti^+ and V^+ and the second-row Nb^+, this amine again demonstrated the preference of these ions for C–H activation, with dehydrogenations and combined losses of H_2 with other neutral particles observed [141]. Cr^+ and Mn^+ formed adduct complexes but dehydrogenation was simultaneously present in unspecified amounts. With Fe^+, Co^+, and Ni^+, in addition to loss of H_2, CH_4 and C_2H_4 were evidence for the ability of these ions to activate C–C bonds as well [141]. In all cases, however, radical losses were encountered too, so that it is very likely that at least part of the metal ions formed were kinetically or electronically excited. This conclusion is further supported by comparison of the reactions of Co^+ with $C_2H_5NH_2$, which have also been studied under ICR conditions [139]. In this case, CoH was the predominant product in addition to H_2 and CH_4. For the labeled $C_2H_5ND_2$, HD was formed in the dehydrogenation which was interpreted as imine-complex formation by way of initial N–D insertion followed by β-H shift and reductive elimination of HD.

Propylamine is the most studied amine with regard to its gas-phase chemistry with bare metal ions. Cr^+ has been found to dehydrogenate this substrate in an ICR instrument, and the same has been claimed for Cu^+ [7(b),142]. This latter finding could not, however, be reproduced in FTICR or sector MS experiments, where CuH accounted for >99% of the products [143]. Here, only loss of CuH could be noted, a product not given in ref. 142 which lists only metal-containing products. Mn^+ and Zn^+ were found to be unreactive toward *n*-$C_3H_7NH_2$ [7(b),142], similar to many other substrates [1]. Fe^+, Co^+, and Ni^+ have been studied with propylamine in an ICR instrument [7(b),139,142] as well as with a sector instrument in metastable ion studies that also included ^{2}H-labeled isotopomers [144,145]. With the latter technique, four products were observed for Fe^+, H_2, NH_3, C_2H_4, and C_3H_6, while in the ICR was noted in addition loss of CH_2 (!) and CH_4. These two products could, however, not be found with an FTICR instrument [146]. The dehydrogenation, which by plausibility arguments was assumed to afford imine complexes [7(b),142], could be shown by the labeling results to proceed in fact by remote functionalization (cf. Scheme 6); the hydrogen was exclusively provided by the β and γ position of the substrate [144,145]. Although the formation of NH_3, C_2H_4 and C_3H_6 was described in terms of simple insertion/β-H shift/competitive ligand loss sequences, the labeling results were inconsistent with this contention. The MI spectra could, however, be explained by the mechanism given in Scheme 16.



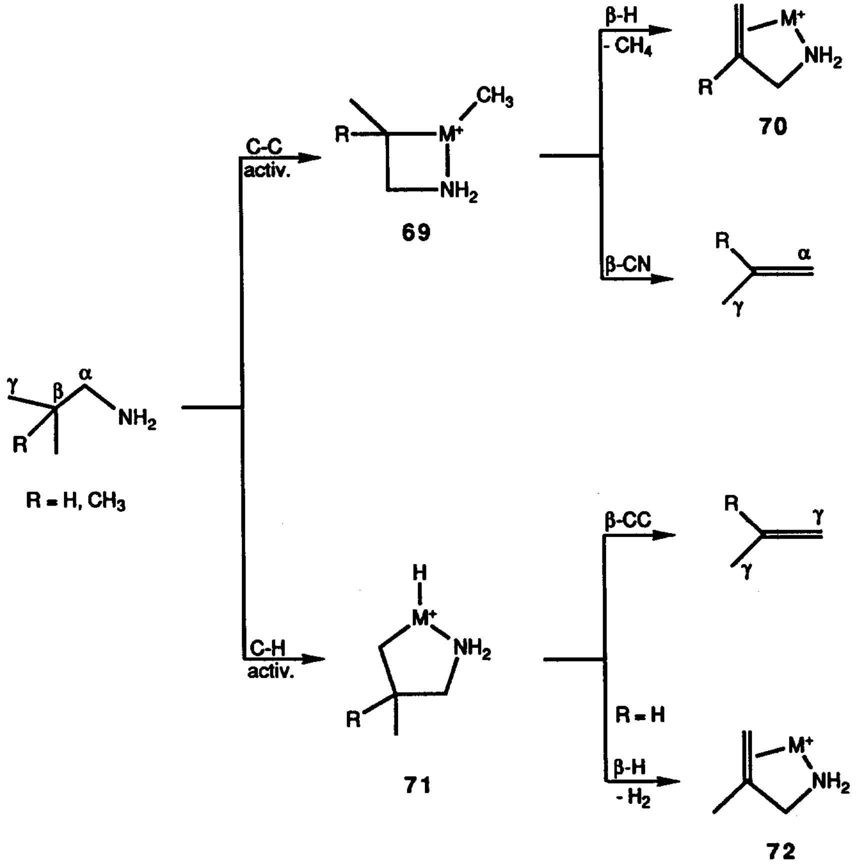
Scheme 16. Generation of ethene, propene, and ammonia in the reaction of Fe^+ with propylamine; equilibration of the α and β position precedes all neutral losses.

Ethene was produced from the internal positions by initial C—C insertion and subsequent C—N cleavage. The immediate precursor for the C_2H_4 loss, complex **66**, also rearranges to **67** in which the two internal carbon atoms are now completely equilibrated due to their prior equivalency in **66** (given facile rotation of the C_2H_4 ligand). The intermediate **67** undergoes the expected β-hydrogen shift to produce NH_3 and C_3H_6.

MI spectra of $Co(n\text{-}C_3H_7NH_2)^+$ complexes showed loss of H_2, C_2H_4, and CoH [144,145] while under ICR and FTICR conditions double dehydrogenation was also observed [7(b),139,142,143]. The labeling studies showed that dehydrogenation was due to remote functionalization, just as for Fe^+, but in this case ethene was formed by the same mechanism, namely from the β/γ position. Scrambling of the "ethyl hydrogens" preceding ethene loss was active but this has precedence in the substituted and unsubstituted butanenitriles (cf. Sect. D(i)). Cobalt hydride formation was specific and involved exclusively the α position to generate the stable immonium ions. While under ICR conditions C_2H_4 was the only reported product for the reaction of Ni^+ with $n\text{-}C_3H_7NH_2$ [7(b),142], MI spectra also revealed loss of H_2 and NiH in smaller amounts [145]. Similar to Co^+, C_2H_4 was formed by remote functionalization and NiH with concomitant immonium-ion generation. Dehydrogenation in the case of Ni^+ was unspecific, however, and involved all four positions.

Isopropylamine has only been studied with Co^+ and afforded mainly H_2 together with equal amounts of CH_4 and CoH [139]. Butylamine with Fe^+ yielded mainly H_2 by remote functionalization in addition to a small amount of C_2H_4, which seemed to be generated by two different mechanisms [147]. While n-$BuNH_2$, i-$BuNH_2$, and *sec*-$BuNH_2$ with Co^+ formed a variety of different products under ICR conditions, including H_2, $2H_2$, CH_4, C_2H_4, C_3H_6, and CoH, t-$BuNH_2$ exclusively afforded CH_4 [139]. Ag^+ with 1-methyl-1-propylamine (*sec*-$BuNH_2$) yielded AgH as the sole product [148]. 2-Methyl-1-propylamine (i-$BuNH_2$) has also been studied in a sector instrument with Fe^+, Co^+ and Ni^+, and here fewer products were observed [149], as compared with the ICR study, which can be ascribed to the well-known tendency of ICR and FTICR studies to show higher amounts of multiple losses [27–31]. As already observed for propylamine, dehydrogenation of i-$BuNH_2$ was specific for Fe^+ and Co^+ and proceeded by remote functionalization while Ni^+ gave rise to extensive scrambling processes [149]. Methane was formed by the mechanism in Scheme 17 ($R = H$) by initial C–C activation followed by β-H shift for all three metal ions. The same mechanism applied for 2,2-dimethyl-1-propylamine (*neo*-$C_5H_{11}NH_2$, $R = CH_3$) in the case of Fe^+–Ni^+ [149]. Loss of C_3H_6 from isobutylamine and of C_4H_8 from neopentylamine was, depending on the metal ion, due to different mechanisms. As depicted in Scheme 17, the initial C–C (**69**) or C–H (**71**) activation products decompose by cleavage of a bond in the β position. While Co^+ and Ni^+ reacted exclusively via the C–H insertion sequence, Fe^+ was able to react in *both* ways [149].

Fe^+ and Co^+ have also been studied with the isomeric substrates 2-ethyl-1-butylamine and 2,2-dimethyl-1-butylamine and several of their isotopomers [147,150]. The main product for Fe^+ reacting with both amines was H_2 which was formed by remote functionalization. In addition to this, butene loss was noted in both cases. For this loss, the mechanism in Scheme 18 was proposed in which initial C–C insertion was followed by β-C–C cleavage to generate either 1-butene or isobutene [147,150]. Quite similarly, t-$PentNH_2$, upon reaction with Fe^+ or Co^+, also loses i-C_4H_8 by insertion into the terminal C–CH_3 bond and β-C–N cleavage to generate CH_3–M^+–NH_2, whose structures have been characterized in CID experiments [146]. Co^+ with 2-ethyl-1-butylamine and 2,2-dimethyl-1-butylamine also afforded H_2 by remote functionalization and C_4H_8 by the mechanism in

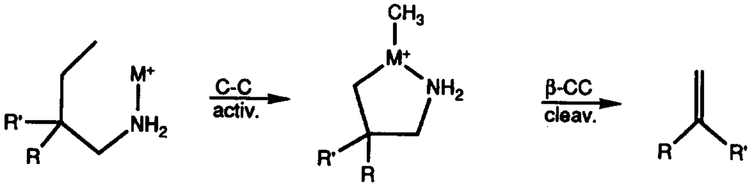


Scheme 17. Generalized mechanism for the C—C and C—H activation of isobutylamine (R = H) and neopentylamine (R = CH_3) by Fe^+–Ni^+.

Scheme 18, but in addition also produced CH_4, C_2H_4, and C_2H_6. Ethene was also formed by remote functionalization while both methane and ethane arose from C—C insertions that were followed by β-H shifts and reductive alkane eliminations.

(iv) Alcohols

Methanol is relatively unreactive with bare metal ions, similar to other C_1 compounds. Only with early and second- or third-row transition-metal ions have bond activations been observed so far. It was, however, claimed in early ICR studies that Fe^+ reacted with CH_3OH to form $FeOH^+$ [38,151], but this result could not be reproduced in a later FTICR study [152], so that very likely electronically excited metal ions were formed under the electron-impact conditions employed [153]. $Fe(CH_3OH)^+$ complexes [154], formed in a CI source, were also found not to



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R = H, R' = C_2H_5
R = R' = CH_3

Scheme 18. Generalized mechanism for the butene loss in the reactions of Fe^+ and Co^+ with 2-ethyl-1-butylamine (R = H, R' = C_2H_5) and 2,2-dimethyl-1-butylamine (R = R' = CH_3).

decompose by unimolecular pathways [155]. Ti^+ forms four ions in the reaction with CH_3OH, with $TiOH^+$ accounting for more than 50% of the products; other losses seen were $H\cdot$, H_2, and CH_4 [124(b)]. Cr^+ [23(c),152], Cu^+ [156] and Ag^+ [90,156,157] did not react at all or only gave rise to the adduct complex with methanol. Au^+, in addition to the adduct complex, yielded AuH [156], Mo^+ dehydrogenated methanol [152], and Ta^+ afforded $TaOH^+$ and TaO^+ [158]. For Y^+, formation of YO^+ and YOH^+ has been reported for quite a variety of different alcohols [159].

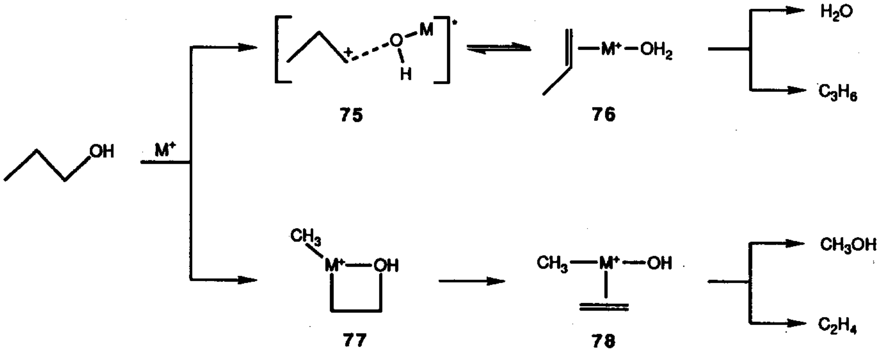
Ethanol is cleaved into ethene and water by Fe^+ [38,152,155] and Co^+ [38], according to the reactions

$$M^+ + C_2H_5OH \rightarrow M(C_2H_4) + H_2O \qquad (14)$$

$$\rightarrow M(H_2O)^+ + C_2H_4 \qquad (15)$$

Ni^+, in addition to the products from reactions (14) and (15), also afforded a small amount of H_2 loss [38], and for Cu^+ dehydrogenation was even the dominant product together with the adduct complex [156,157]. H_2 loss was also observed for Pd^+ [138], and the very reactive Mo^+ even gave rise to single and *double* dehydrogenation of C_2H_5OH [152]. On the other hand, Cr^+ [152], Mn^+ [53], and Ag^+ [90,156,157] were unreactive with this alcohol, and Au^+ afforded mainly AuH and some H_2O loss [156]. Using labeled ethanol isotopomers, it could be shown that hydride abstraction involved the α position as in the case of the amines and that dehydration occurred in a 1,2 manner without scrambling. As demonstrated by high-resolution FTICR spectra, Rh^+ generated among others the isobaric $RhCO^+$ and $RhC_2H_4^+$ ions from C_2H_5OH [4(e),129(d)].

The gas-phase chemistry of propanol is already much more versatile than that of its lower homologues. There are also differences, in some cases, in product distributions between different instruments where the same system was studied. While $Fe(n\text{-}C_3H_7OH)^+$ complexes in MI spectra exclusively lost H_2O [145,155], under FTICR conditions Fe^+ also formed additional products, although here too, dehydration was the main reaction [152]; besides the rare loss of a $CH_3\cdot$ radical, C_2H_4 and C_3H_6 were observed. In MI experiments, Co^+ formed mainly H_2O in addition to C_3H_6, C_2H_4 and CH_3OH [145] while in an ICR study, loss of H_2O, C_3H_6, C_2H_4, and CH_4 were noted besides the adduct complex [160]. Ni^+ formed the same products as did Co^+, but in different intensities and together with some dehydrogenation products [145]. Mechanistically, formation of H_2O and C_3H_6 has been described with an insertion/β-H shift mechanism [152,160]. The results of ^2H-labeled propanols [145,155], however, make it obvious that this simple picture does not hold further. For all three ions (Fe^+–Ni^+), hydrogen atoms from all positions, including the OH proton, contribute to the H_2O loss, and for the corresponding C_3H_6 loss, scrambling is noted too. As outlined in the preceding sections, scrambling can be an indication that the ion/dipole mechanism is operative. It is therefore proposed in this article that cleavage of propanol, and very likely other alcohols as well, to H_2O and an alkene proceeds via the ion/dipole mechanism (Scheme 19).



Scheme 19. Formation of H_2O and C_3H_6 from propanol via the ion/dipole mechanism and of C_2H_4 and CH_3OH via initial C—C insertion.

The labeling results [145] also revealed the origin of the C_2H_4 and CH_3OH molecules that were formed from propanol in the reactions of Co^+ and Ni^+ and in case of Fe^+ under FTICR conditions. For Co^+, the reaction was highly specific and proceeded in strict analogy to the C_2H_4 loss from propylamine in Scheme 16 [145]. The same result was obtained for the reaction of Fe^+ with $CD_3CH_2CH_2OH$ *in an ion source* or in high-energy CID experiments [161]. The structure of the resulting CH_3–Fe^+–OH ion was distinguished from other $FeCH_4O^+$ isomers by means of CID [154]. For Ni^+, the formation of C_2H_4 and CH_3OH was more complex and involved only ca. 20% the sequence in Scheme 19. The dehydrogenation observed with this ion was also unspecific and involved all four positions of the substrate [145]. H_2 loss was also observed frequently with other ions; for Cr^+, this was the sole product under FTICR conditions, and Mo^+ even doubly and triply dehydrogenated *n*-PrOH [152]. In an ion-beam study, Cr^+, besides H_2 also yielded C_2H_4 and C_3H_6 at 0.5 eV kinetic energy [162]. For Cu^+, H_2 was the predominant product together with CuH, H_2O, and C_3H_6, and even for Ag^+, dehydrogenation was observed to a small extent [90,156,157]. For Au^+, however, this reaction was absent, and AuH was once more the main product in addition to H_2O, C_3H_6, and AuOH [156].

For isopropanol, the cleavage into C_3H_6 and H_2O is more important than for *n*-propanol. This finding is completely in line with the proposed operation of the ion/dipole mechanism. The rupture of the C–O bond is facilitated by the formation of the more stable incipient 2-propyl cation, and alternative mechanisms such as remote functionalization are, on the other hand, disfavored or even impossible due to the small chain length. Of course, the possibility of an insertion mechanism cannot be excluded with certainty. It is not surprising that Fe^+ [38,152,163], Co^+ [38], and Ni^+ [38] predominantly react to form $M(C_3H_6)^+$ and $M(H_2O)^+$, but the fact that Cr^+ [152,162], Cu^+ [156,157], Au [156], and Mo^+ [152] to a signficant degree do the same makes it unlikely that the insertion/β-H shift sequence applies. Heterolytic C–O cleavage has been previously suggested for metal ions with limited insertion abilities such as Cr^+ [162] or the group 11 ions [156,157]. Dehydrogenation was seen for Cr^+ [152,162], Cu^+ [156,157], Ag^+ [90,156], and in double and triple form for Mo^+ [152]. Other products noted were due to abstraction reactions and led to CuH, AuH, $AuCH_3$, and AuOH [156].

Reactions of higher alcohols proceeded similarly to the ones described so far. In the case of Fe^+, MI [155,164] and FTICR [152] results showed similar trends if the pronounced tendency for multiple losses in the latter approach is accounted for. Loss of H_2O was insignificant for linear alcohols but was more important for branched isomers. The MI studies [155,164] revealed that loss of H_2 was the dominant product for all *n*-alkanols from butanol through decanol. Also, loss of C_2H_4 and higher alkenes was observed too. Labeling studies on 1-pentanol showed that indeed, as suspected, remote functionalization was operative in the loss of H_2 and of C_2H_4. In view of the increasing amounts of higher alkenes that were produced with greater chain length of the alcohols, it is very likely that these are formed by the same mechanism via initial insertions into $(\omega - 1)$, $(\omega - 2)$, ... C–H bonds (cf. Scheme 6). In the FTICR study, the relative amount of H_2 decreased for the higher alcohols and losses of C_nH_{2n+2} became more important [152]. These were formulated as alkane losses via C–C insertions/β-H shifts/reductive eliminations. The discrepancy can be readily explained, however, if it is assumed that these "alkanes" are in fact combined losses of alkenes and H_2. For the analogous Co^+ system, this could indeed be demonstrated using some labeled hexanols [165]. Here, loss of C_2H_6 was already observed in MI spectra and was found to be due to combined C_2H_4/H_2 loss. Co^+-induced loss of H_2 and C_2H_4 from 1-pentanol [164] and 1-hexanol [165] was due to remote functionalization; in particular, the formation of aldehydes or the activation of the O–H bond in general, which was previously suggested [152,160,166], could be excluded. In general, Co^+ showed a higher amount of dehydration and less dehydrogenation than did Fe^+, and alkenes were the dominant products for alcohols longer than butanol [164]. Also observed with Co^+ were losses of smaller alcohols [160,164,166]. To explain the observed product distributions, 5- or 6-membered ring intermediates *preceding* C—C insertions have been postulated, yet no labeling is available that would substantiate this proposal [160,164].

With larger linear alcohols Cr^+ mainly afforded C—C activation products, alkanes and alkenes, while branched alcohols predominantly underwent H_2O loss [152]. As already noted above, this supports the operation of the ion/dipole mechanism for this process. For Mo^+ the loss of H_2O/H_2 was the most important loss for *t*-BuOH; the other alcohols were mostly multiply dehydrogenated [152]. While *n*-butanol was still dehydrogenated by Cu^+, the most important process, as for the other isomers, was still cleavage into H_2O and butene [156], and even Ag^+ was able to induce H_2O loss from *t*-BuOH [90,156,157]. For Au^+, however, AuH from *n*- and i-BuOH, $AuCH_3$ from *t*-BuOH, as well as AuOH from all three isomers continued to be the most important products [156].

(v) Alkyl halides

With the exception of Au^+ (see below), only two reactions have been observed for methyl halides, viz.

$$M^+ + CH_3X \rightarrow MX^+ + CH_3\cdot \tag{16}$$

$$\rightarrow MCH_3^+ + X\cdot \tag{17}$$

For $M^+ = Ti^+$, reaction (16) is the only one observed for all four halides (X = F, Cl, Br, I) [167,168], and the same applies for $M^+ = Cu^+$ and CH_3Cl [77] and Cr^+ and Hg^+ in case of CH_3I [151]. For Fe^+ and Co^+, both reactions have been observed for methyl iodide [37,38,151], and this has, in fact, been taken as an indication that transition-metal ions were able to insert into R—X bonds. The necessary $CH_3{-}Fe^+{-}I$ intermediate could, in fact, be generated in a ligand-exchange reaction (18) and was found to be different from $Fe(CH_3I)^+$ as reaction (19) excluded a "symmetrical" $[(CH_3I)Fe^+(ICD_3)]^*$ intermediate/collision complex from which equally intense losses of $CH_3\cdot$ and $CD_3\cdot$ would be expected [38,151].

$$Fe(CO)^+ + CH_3I \rightarrow FeCH_3I^+ + CO \tag{18}$$

$$FeCH_3I^+ + CD_3I \rightarrow FeCD_3I_2^+ + CH_3\cdot \tag{19}$$

Ni^+ only formed NiI^+ in reaction (16) [38,151], and with CH_3Br the metal bromides were the only products for Fe^+–Ni^+ [37,38]. A careful examination of the reactions of Fe^+, Co^+, and Ni^+ with CH_3Cl, CH_3Br, and CH_3I in an ion-beam instrument allowed bond energies $D^0(M^+{-}X)$ and $D^0(M^+{-}CH_3)$ to be derived from the analysis of the cross-sections [153,169]. It was found that MCH_3^+ formation was endothermic in all cases except for $FeCH_3^+$ from CH_3I. Observation of $CoCH_3^+$ from CH_3I [37,38,151] was shown to be due to the first excited ^5F state formed under the electron-impact conditions used in the earlier studies. MCl^+ formation was endothermic for Co^+ and Ni^+ [169] but exothermic for Fe^+ [153], and the reactions to MBr^+ and MI^+ were exothermic in all cases. Two distinct mechanisms were operative, as could be shown from features of the cross-section; at low energies, $CH_3–M^+–X$ intermediates were formed that decomposed to the two observed products. At higher kinetic energies, a second path became available that led to direct abstraction of X, and not CH_3, but a barrier had to be overcome for this process [153,169]. Au^+ again demonstrated a radically different behavior toward the methyl halides; only for CH_3I, reactions (16) and (17), H^- abstraction and HX elimination were observed [91]. For CH_3Cl and CH_3Br, the HX elimination with concomitant $AuCH_2^+$ formation was the predominant process.

The high affinity of Ti^+ to halogens can also be seen with ethyl and isopropyl chloride where $Cl\cdot$ and Cl^- abstraction is the only chemistry observed [168]. With Mn^+, Cl^- abstraction together with HCl elimination and formation of alkene complexes were observed for n-C_3H_7Cl, i-C_3H_7Cl, and i-C_4H_9Cl [53]. The chemistry of Fe^+ [37,38,151], Co^+ [37,38,151,160,166], and Ni^+ [38,151] with alkyl halides is again very similar and related to that with alcohols. With smaller substrates, halogen abstraction and cleavage into HX and alkenes was found while for larger chlorides loss of smaller alkenes or alkyl chlorides was also present. The latter processes have been formulated as being due to C–C activation arising from preformed 5- or 6-ring intermediates [160] and were modelled theoretically with the Cr^+/n-C_4H_9Cl system [170]. Statistical loss of HI and DI from Fe^+/CD_3CH_2I was interpreted by C–I insertion followed by reversible β-H shifts [38,151], but this finding can, of course, also be taken as an indication for ion/dipole intermediates showing H scrambling in the incipient carbenium ions. While ethyl chloride reacted only to $M(HCl)^+$ and $M(C_2H_4)^+$ with Cu^+ [77] and Ag^+ [157], for larger alkyl chlorides halide abstraction with simultaneous carbenium-ion formation was also observed and was, in fact, often the main product channel for both ions [16,77,157].

(vi) Miscellaneous substrates

Thiols show a higher reactivity than their oxygen analogues; already methanethiol, CH_3SH, formed NiS^+ upon reaction with Ni^+ [129(b),(c)]. Metal sulfide ions, in addition to H_2 loss, were also obtained from the reactions of Ti^+ and V^+ with ethanethiol [4(a)]. Fe^+ formed only H_2S from this thiol while Co^+ was reported to afford CH_4, C_2H_4, and H_2S [4(a)]. In another study on Co^+, methane loss was not observed for this particular system [171]. The majority of the products formed from Co^+ reacting with alkanethiols stemmed from C–S cleavage, and loss of H_2S together with $Co(H_2S)^+$ formation accounted for the main part of the ions formed [171]. They were occasionally accompanied by SH^- abstraction, and, in the case of n- and *sec*-BuSH, loss of H_2S/H_2 could be noted, obviously driven by the formation of stable butadiene complexes. C–C cleavage products were usually of minor importance. All products were again explained with insertion/β-H shift mechanisms but can, of course, also be explained by the ion/dipole mechanism. This latter assumption gets further credence from a recent study of Cu^+ and Ag^+ with propanethiol and the four isomeric butanethiols [172]. Besides $M(H_2S)^+$ by loss of alkenes and $M(alkene)^+$ by loss of H_2S, $C_4H_9^+$ ions were formed. Secondary reactions afforded adduct complexes in all cases. Again, for thiols there seems to be no difference between these d^{10} ions and Fe^+–Ni^+ with regard to the cleavage into H_2S and alkenes.

The last class of substrates to be presented here are nitroalkanes. Mn^+ [53], Ni^+ [173], Cu^+ [173], and Ag^+ [173] were unreactive with nitromethane, CH_3NO_2; products were, however, observed for Fe^+ [173], Co^+ [173,174], Rh^+ [173], and Pd^+ [173]. Using Fe^+ and Co^+, mainly $MOCH_3^+$ ions were obtained for which a nitro-to-nitrite isomerization was postulated. Other important products were MO^+ and MOH^+ ions, and altogether 8 (Fe^+) and 11 (Co^+) products were formed. Interestingly, thermal and photochemical isomerizations of nitroalkanes to alkyl nitrites are believed to occur by NO_2 dissociation from the alkyl group followed by recombination [174]. For the two second-row ions, MNO^+ ions were the sole products and were also believed to be formed after rearrangement to methyl nitrite. Other nitroalkanes have only been studied with Fe^+, Co^+, and Ni^+ [174,175]. A plethora of products was always formed, and many of them were also explained by isomerizations; insertions into C–H, C–C, C–N, and N–O bonds were postulated to account for the individual product ions. Among the products were always $M(alkene)^+$ ions by loss of HNO_2, $MHNO_2^+$ ions by loss of an alkene and, commencing with $C_3H_7NO_2$, also carbenium ions by NO_2^- abstraction. These latter drastically gain in importance for branched nitroalkanes and are furthermore most abundant for Ni^+. Although these three products were explained with C–NO_2 insertions followed by β-hydrogen shifts, the reader will undoubtedly recognize the now all-too-familiar pattern of the ion/dipole mechanism which is hence proposed here to be operative for nitroalkanes as well. This interpretation would also account for the nitro-to-nitrite isomerization which is observed for CH_3NO_2 and with decreasing importance for higher homologues; initial NO_2^- abstraction could be followed by recombination to form nitrite complexes.

Some other representatives of monosubstituted alkanes have also been studied but there is insufficient data available for a generalizing presentation. The interested reader is referred to ref. 1 for a detailed account.

E. SUMMARY AND CONCLUSIONS

This review has tried to give a comprehensive description of the gas-phase chemistry of monosubstituted alkanes $C_nH_{2n+2}X$ with bare metal ions M^+, generated in different kinds of research mass spectrometers. Regardless of the instrumentation employed (ICR, FTICR, sector, or ion-beam machines), or the nature of M^+ (main-group or transition-metal ions) or X, some common observations emerge. If the substrate is either small, so that some mechanisms are excluded simply because of lack of a minimum size, or the metal ion is relatively unreactive, i.e. unable to undergo oxidative additions or not very inclined to do so, as in case of alkali-metal ions or closed d^{10} or half-closed d^5 configurations of transition-metal ions, reactivity may nevertheless be observed. Frequently, reactions (20)–(22) are encountered in these cases.

$$M^+ + RX \rightarrow R^+ + MX \tag{20}$$

$$\rightarrow M(HX)^+ + \text{alkene} \tag{21}$$

$$\rightarrow M(\text{alkene})^+ + HX \tag{22}$$

Depending on M^+ and RX, different mechanisms have been proposed to account for the products formed. It is the purpose of this article to further the idea of a common mechanism, though, namely the ion/dipole mechanism in Schemes 9 and 10. Coordination of M^+ to a lone pair on X leads to heterolytic cleavage of the C–X bond and the formation of a complex consisting of a carbenium ion and neutral XM. If the energetics are favorable, dissociation of the intermediate complex may occur to afford the products of reaction (20). Subsequent protonation of the X atom in the metal-containing dipole yields a new complex in which the metal ion is coordinated to an HX and an alkene ligand. Finally, competitive ligand loss from this intermediate furnishes the products in reactions (21) and (22). Noteworthy is the absence of any oxidative-addition step in this scenario.

As demonstrated most convincingly for nitriles and isonitriles, many arguments add together in support of this mechanism. Unfortunately, for other substrates the structure of $M(HX)^+$ or HX cannot be established as straightforwardly as for $M(HCN)^+$ and $M(HNC)^+$ or is inconclusive with regard to mechanistic alternatives. Other indications may, however, be more frequently observed, e.g. hydrogen scrambling beyond the β-positions of the substrates, a process most simply explained by rapid 1.2-H shifts in the incipient carbenium ions in the ion/dipole intermediate $[R^+ \cdots XM]^*$. Another strong point in support of the mechanism is the observation of a common behavior for transition-metal ions that, in principle, could react via an insertion/β-H shift path (e.g. Fe^+–Ni^+) and those that are unable to do so (e.g. Li^+, Na^+, Cr^+, Cu^+). Both tests, scrambling and common behavior of distinct ions, have been applied in the case of isocyanates and isothiocyanates to demonstrate the operation of the ion/dipole mechanism. Published data for other substrates such as alcohols, alkyl halides, thiols, or nitroalkanes have also been critically examined and presented in light of the knowledge about the mechanism. For several cases the ion/dipole mechanism has been proposed in this article to be operative, and this has been done in view of the many similarities to the cases where its operation could be convincingly demonstrated. It remains to be proven, however, whether this conclusion indeed holds true for all systems. Yet, the use of secondary reactions to dispute its operation does not withstand critical examination. The different results obtained for Cr^+–Zn^+ with different isocyanates should caution anyone not to put too much emphasis on the outcome of ligand-substitution reactions.

Of course, the ion/dipole mechanism is far from being the only mechanism that is operative in gas-phase organometallic chemistry. Frequently observed is also the remote functionalization of unactivated C–H bonds (Scheme 6). Here, coordination of the metal ion to X prevents it from reaching nearby bonds, and thus remote C–H bonds are oxidatively added and eventually lead to the production of H_2 and alkenes from distant positions. Early transition-metal ions, as well as many second- or third-row ions, often give rise to (multiple) dehydrogenations of the substrate or show losses of H_2 together with other small neutrals, thus demonstrating their preference for C–H activations. Other special mechanisms have been observed for different systems but so far no other generalization seems warranted.

It is hoped that researchers will apply the criteria given in this review to their own systems and find some common features. The time when every new system brings up some surprising results does not seem to be completely over, though.

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