26. Dehydrosulfurization of Isothiocyanates by Gas-Phase Fe(I) Cations

by **Karsten Eller**, **Semiha Akkök**, and **Helmut Schwarz***

Institut für Organische Chemie der Technischen Universität Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12

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Bare Fe(I) cations act in the gas phase as dehydrosulfurization catalysts for butyl isothiocyanate by specifically coupling the S-atom with remote H-atoms from the ω and $(\omega - 1)$ position of the alkyl chain. Other losses induced by Fe(I) are due to 'remote functionalization', the formation of ion/dipole intermediates, and insertion/β-hydrogen shift processes.

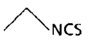
Introduction. – Catalytic *hydrode*sulfurization (HDS) is a very important process in the petroleum and petrochemical industry. In fact, the removal of sulfur from crude oils and coal liquids by conversion of the organic sulfur content to H_2S is one of the largest-scale chemical processes [1]. For this hydrogenolytic reaction, the catalysts used in industry are normally derived from oxides of group-VI elements (Mo, W), promoted with either Co or Ni, and supported on γ-alumina, that are *in situ* persulfided with H_2S/H_2 [2]. In view of the industrial importance of HDS, it is no wonder that a better understanding of the basic principles of this process and development of improved catalysts are an area of intense research [3].

One approach to study the *intrinsic* properties of the catalytically active sites, *i.e.* the transition-metal atoms or ions, is to investigate the reactions of bare or ligated metal ions with organic model substrates in the gas phase. Gas-phase studies are not hampered with the problems of solvation, ion pairing, or ligand effects that strongly influence the condensed-phase studies on catalysis [4], and it is, thus, not surprising that organometallic chemistry in the gas phase has developed to an actively pursued topic (for reviews, see [5]). The rapidly growing data nowadays allows a much better understanding of the principles and mechanisms of C–H and/or C–C bond activation, and we, therefore, decided to investigate the influence that a S-atom exerts on the reactivity of monofunctional substrates in their reactions with bare metal ions, also in the hope to learn more about the mechanisms of HDS.

Although it is well known that the presence of sulfur can have substantial effects on the performance of catalysts, by, for example, poisoning the isomerization or hydrogenation properties [6], it has so far received little attention in either condensed-phase catalysis [7] or gas-phase studies. *Freiser* and coworkers have studied the reactions of a few transition-metal cations with ethylene sulfide, which led to the formation of metal polysulfide ions [8], the chemistry of transition-metal anions with simple thiols, sulfides, and disulfides [9], and of MS^+ ions (M = Fe, Co, Ni) with alkanes [10]. Finally, the reactions of Fe^+, Co^+, and Ni^+ with thiols and sulfides have been studied by *Carlin* [11] and *Lombarski* and *Allison* [12].

Results and Discussion. – The reactions of aliphatic cyanides with various metal ions have been studied by our group in great detail [5k,m,n], as have been those of the corresponding isocyanides [13]. The introduction of sulfur into the molecules by choosing isothiocyanates, therefore, seemed to be appropriate. As preliminary studies on the first members of the row of alkyl isothiocyanates quickly revealed that a drastic change in behaviour occurs at a chain length of four C-atoms, we will only briefly discuss the reactions of ethyl isothiocyanate (**1**) and propyl isothiocyanate (**2**) with gas-phase Fe^+, as the more detailed discussion on the butyl isothiocyanate (**3**) system will demonstrate the basic principles more clearly.

The metastable-ion (MI) decompositions of the complexes **1**-Fe^+ and **2**-Fe^+ (see *Exper. Part* for details) are given in *Eqns. 1* and *2*. The relative extent of *dehydro* sulfurization, *i.e.* loss of H_2S, is always a minor process which accounts only for 1 and 2%, respectively, of the products formed. However, the extent of this process *drastically* increases in going over to the Fe(I)-complexed BuNCS (**3**-Fe^+, *Eqn. 3*); the loss of H_2S in this system represents the major decomposition pathway. As metastable-ion studies indicate those processes that are energetically the least demanding [14], the facile dehydrosulfurization of **3**-Fe^+ points to a very special situation. As the chain length exerted this tremendous influence, the idea arose that perhaps remote positions of the chain were serving as an internal H_2 source for the hydrogenolytic removal of the sulfur. This was insofar supported, as **3**-Fe^+ also was the first system in this series to show loss of H_2. To test this hypothesis, the labeled compounds **3a**–**c** were synthesized and their gas-phase reactions with Fe^+ studied.



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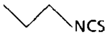

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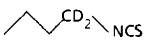
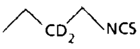
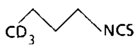


3a



3b



3c

$$\mathrm{Fe(C_2H_5NCS)^+} \xrightarrow{\mathrm{MI}} \left\{ \begin{array}{llll} \xrightarrow{0.96} & \mathrm{Fe(HNCS)^+} & + & \mathrm{C_2H_4} \\ \xrightarrow{0.01} & \mathrm{FeC_2H_3N^+} & + & \mathrm{H_2S} \\ \xrightarrow{0.03} & \mathrm{Fe(C_2H_4)^+} & + & \mathrm{HNCS} \end{array} \right. \qquad (1)$$

$$\mathrm{Fe(C_3H_7NCS)^+} \xrightarrow{\mathrm{MI}} \left\{ \begin{array}{llll} \xrightarrow{0.10} & \mathrm{FeC_3H_6S^+} & + & \mathrm{[HNC]} \\ \xrightarrow{0.07} & \mathrm{FeC_2H_3NS^+} & + & \mathrm{C_2H_4} \\ \xrightarrow{0.02} & \mathrm{FeC_4H_5N^+} & + & \mathrm{H_2S} \\ \xrightarrow{0.70} & \mathrm{Fe(HNCS)^+} & + & \mathrm{C_3H_6} \\ \xrightarrow{0.11} & \mathrm{Fe(C_3H_6)^+} & + & \mathrm{HNCS} \end{array} \right. \qquad (2)$$

$$\mathrm{Fe(C_4H_9NCS)^+} \xrightarrow{\text{MI}} \left\{ \begin{array}{lllll} \xrightarrow{0.17} & \mathrm{FeC_5H_7NS^+} & + & \mathrm{H_2} \\ \xrightarrow{0.07} & \mathrm{FeC_4H_8S^+} & + & \mathrm{[HNC]} \\ \xrightarrow{0.13} & \mathrm{FeC_3H_5NS^+} & + & \mathrm{C_2H_4} \\ \xrightarrow{0.02} & \mathrm{FeC_4H_6S^+} & + & \mathrm{[HNC, H_2]} \\ \xrightarrow{0.35} & \mathrm{FeC_5H_7N^+} & + & \mathrm{H_2S} \\ \xrightarrow{0.04} & \mathrm{FeC_2H_3NS^+} & + & \mathrm{C_3H_6} \\ \xrightarrow{0.15} & \mathrm{Fe(HNCS)^+} & + & \mathrm{C_4H_8} \\ \xrightarrow{0.06} & \mathrm{Fe(C_4H_8)^+} & + & \mathrm{HNCS} \end{array} \right. \tag{3}$$

Loss of Hydrogen. As can be seen from the data in the *Table*, molecular hydrogen is specifically produced from the ω and ($\omega - 1$) position of the chain, except for a very small amount of scrambling ($< 4\%$) that is also observed. This finding is completely in agreement with other results for related systems where it could also be shown that hydrogen originated from these positions; consequently, the dehydrogenation found here represents a further case of '*remote functionalization*'. The process of 'remote functionalization', a concept that was originally introduced by *Breslow* in combination with biomimetic synthesis [15], can be expressed in terms of the general picture given in *Scheme 1*. A transition metal M^+, 'anchored' at the functional group X of the substrate (*cf.* **I**), on

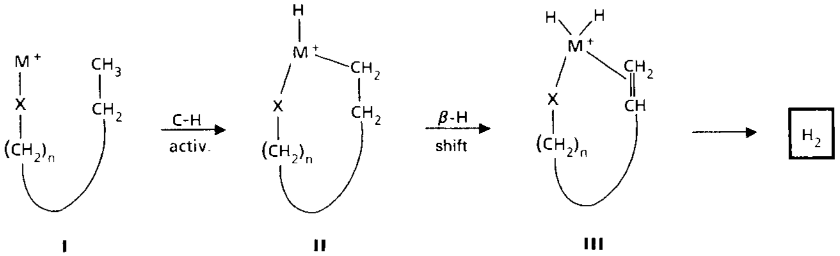
Table. *Reaction Products Arising from the Dissociation of Metastable Fe$^+$ Complexes of Labeled Butyl Isothiocyanates*[a])

Product	$CH_3CH_2CH_2CD_2NCS$ (**3a**)	$CH_3CH_2CD_2CH_2NCS$ (**3b**)	$CD_3CH_2CH_2CH_2NCS$ (**3c**)
H_2	100	97	< 4
HD		3	> 96
H_2S	93	88	10
HDS	7	12	90
C_3H_6	100		
$C_3H_4D_2$		100	
$C_3H_3D_3$			100
$FeHNCS^+$	91	73	83[b])
$FeDNCS^+$	9	27	17[b])
HNCS	90	71	84[b])
DNCS	10	29	16[b])

[a]) Intensities were normalized to 100% for each neutral.

[b]) Calculated according to branching ratio $HNCS/FeHNCS^+$ of unlabeled BuNCS due to isobaric $FeHNCS^+$ and $[M - HNCS]^+$ for **3c**.

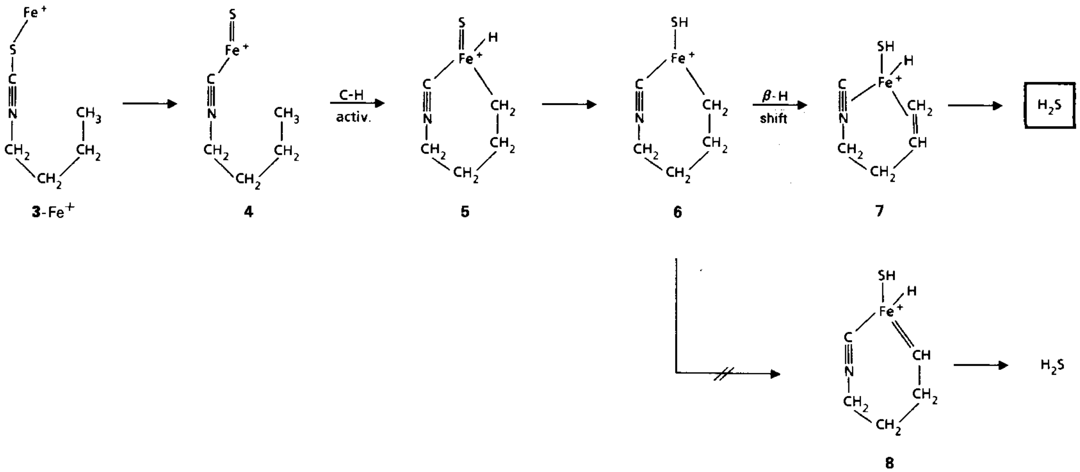
Scheme 1



geometric grounds is only capable of activating the C—H bonds of the remote Me group, thus forming an intermediate metallacycle **II**, which decomposes by β-H shift (**II**→**III**) and reductive elimination of H_2. The functionalization of remote, nonactivated C—H bonds that can be achieved by bare metal ions was first discovered by our group for cyanides [16], but has, in the meantime, also been found for various other systems, such as isocyanides [13], amines [17], ketones [18], and linear, unsaturated hydrocarbons [19], and it can, therefore, be seen as an established, quite generally applicable pathway.

Dehydrosulfurization. More noteworthy, and somehow surprising, is the fact that *ca.* 90% of the H-atoms that are incorporated in the H_2S also originate from the ω and (ω − 1) position. The significantly higher amount of scrambling observed, though, indicates that both products, H_2 and H_2S, *do not arise from a common intermediate.* Two experimental observations might give some hints for a possible mechanism. Firstly, collisional activation experiments of the $[Fe,H,N,C,S]^+$ complexes formed (see below) reveal that cleavage of the N—S bond is a facile process. Secondly, the smallest isocyanide to show dehydrogenation products with Fe^+ is BuNC [13a]. Based upon these observations, we suggest that the mechanism depicted in *Scheme 2* may be a reasonable description for the dehydrosulfurization, and we state that it is at least in accordance with all experimental findings.

Scheme 2

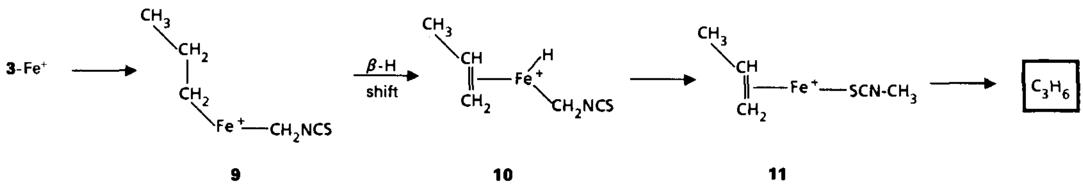


The first step is believed to be either an insertion of the metal ion into the C–S bond, or sulfur abstraction, followed by rearrangement, which would afford the same intermediate **4**. Experimentally, no distinction between these two alternatives is possible so far; there exist, however, precedents for the abstraction of sulfur from the condensed-phase studies. Intermediates that contain a proper leaving group, such as butadiene, supposedly give rise to $S{=}Fe(CO)_4$ in homogeneous or S=Mo(IV) in heterogeneous catalysis [20]. The next step, **4** → **5**, is strictly analogous to **I** → **II**, with X being NC, except that a *ligated* metal ion is involved. One could formulate a step analogous to **II** → **III**, although, in view of the different amount of scrambling observed, the reaction might well proceed by a 1,2-H shift onto the sulfur, **5** → **6** *before* the β-H is transfered (**6** → **7**). In any case, reductive elimination of H_2S from intermediate **7** will terminate the sequence. As (1,1)-elimination products are not observed, the intermediacy of a Fe^+-carbene complex **8** can be ruled out.

The fact that complexes of BuNCO with Fe^+ do *not* show analogous loss of H_2O [21] is not surprising in view of the different bond-dissociation energies involved. While the bond-dissociation energies of Fe^+ to sulfur and oxygen are about the same, $D^\circ_{298}(Fe^+{-}O) = (68 \pm 5)\ \text{kcal}\cdot\text{mol}^{-1}$ [8c][22] and $D^\circ_{298}(Fe^+{-}S) = (65 \pm 5)\ \text{kcal}\cdot\text{mol}^{-1}$ [8c][10], the $D^\circ_{298}(RNC{=}X)$ values are quite different. Oxygen is bonded much stronger than sulfur ($D^\circ_{298}(C_2H_5NC{=}O) = 113.4\ \text{kcal}\cdot\text{mol}^{-1}$, $D^\circ_{298}(C_2H_5NC{=}S) = 80.9\ \text{kcal}\cdot\text{mol}^{-1}$)¹), which makes the insertion much more unfavorable²). This applies, although the overall reaction to generate H_2O is estimated to be 13.8 kcal·mol⁻¹ *more exothermic* than loss of H_2S³).

Loss of Propene. The data in the *Table* leaves no doubt that the formation of propene is a straightforward process that can be described in terms of the common insertion/β-H shift mechanism [27]. Insertion into the C(1)–C(2) bond (**3**-Fe^+ → **9**; *Scheme 3*) is followed by β-H shift (**9** → **10**) and rearrangement to the biligated complex **11**. From **11**, exclusively propene is lost due to the much stronger binding energy of the MeNCS. The same labeling data would result for the reversed sequence of steps, *i.e.*, if the reaction would commence with insertion of the (complexed) Fe^+ ion into the C–H bond of C(3), followed by β-C–C bond cleavage and loss of propene.

Scheme 3



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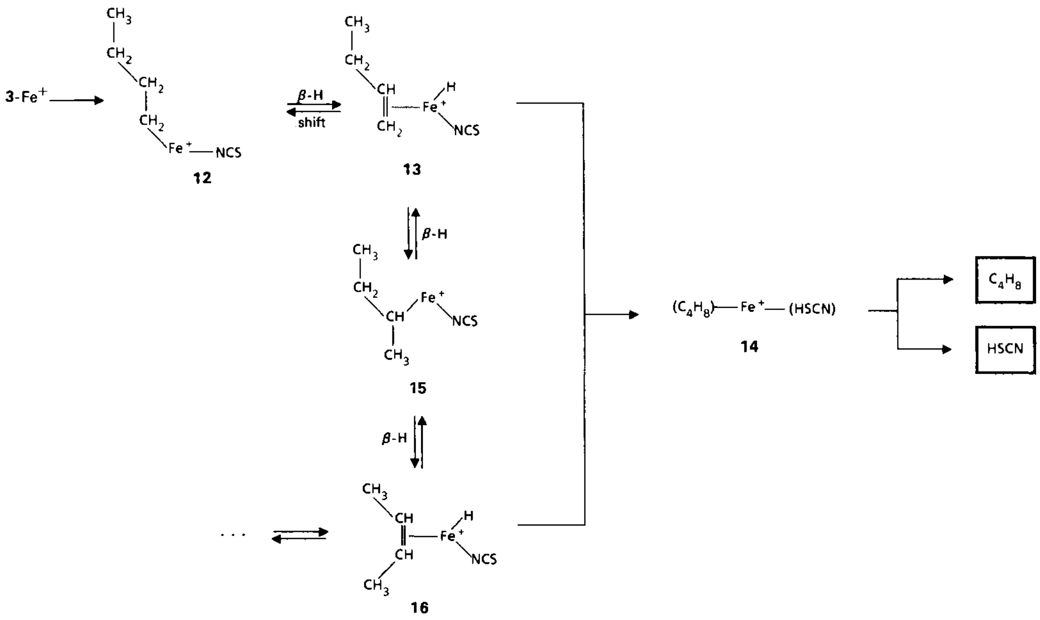
¹) Bond-dissociation energies were estimated from $\Delta H^\circ_f(C_2H_5NC) = 33.5\ \text{kcal}\cdot\text{mol}^{-1}$ [23], $\Delta H^\circ_{f(298)}(O(g)) = 59.553\ \text{kcal}\cdot\text{mol}^{-1}$ [24], $\Delta H^\circ_{f(298)}(S(g)) = 66.20\ \text{kcal}\cdot\text{mol}^{-1}$ [24], $\Delta H^\circ_{f(298)}(C_2H_5NCO(g)) = -20.3\ \text{kcal}\cdot\text{mol}^{-1}$ [25], and $\Delta H^\circ_{f(298)}(C_2H_5NCS(g)) = 18.8\ \text{kcal}\cdot\text{mol}^{-1}$ [25].

²) Recently, a higher value for $D^\circ_{298}(Fe^+{-}O) = (81 \pm 1)\ \text{kcal}\cdot\text{mol}^{-1}$ has been reported [26], but insertion would still be disfavored.

³) Based upon $\Delta H^\circ_{f(298)}(H_2O(g)) = -57.796\ \text{kcal}\cdot\text{mol}^{-1}$ [24] and $\Delta H^\circ_{f(298)}(H_2S(g)) = -4.93\ \text{kcal}\cdot\text{mol}^{-1}$ [24].

Scheme 4



Loss of [H,NCS] and Formation of [Fe,H,N,C,S]$^+$ Complexes. From all labeled isothiocyanates, a mixture of [H,NCS] and [D,NCS] as well as of [Fe,H,N,C,S]$^+$ and [Fe,D,N,C,S]$^+$ complexes is formed. The branching ratio, that is identical within experimental uncertainties for the respective isotopomers, provides evidence for a common intermediate for both products. It is tempting to describe their formation again in terms of the insertion/β-H shift mechanism [27] as depicted in *Scheme 4*, with **14** being the common intermediate. To account for the scrambling observed, one would on the other hand be forced to postulate reversible β-H shifts (**13**⇆**15**⇆**16** ...). A more likely explanation can, however, be obtained, if one assumes that this reaction represents another example of the ion/dipole mechanism[4]), which was first observed for secondary and tertiary nitriles [30], and which seems to be operative for isocyanides [13b] and tertiary amines [31] as well. A brief description of the (*t*-Bu)NC–Fe$^+$/(*t*-Bu)CN–Fe$^+$ system may serve to demonstrate the principles of the ion/dipole mechanism.

With Fe$^+$, both isomers give almost exclusively rise to [H,CN] and [Fe,H,CN]$^+$. It was possible to show that *a*) the initial coordination site of the metal ion is preserved upon reaction to the products HNC–Fe$^+$ from (*t*-Bu)NC and HCN–Fe$^+$ from (*t*-Bu)CN [30a], therefore, excluding an insertion of Fe$^+$ into the CH$_2$–N or CH$_2$–C bond from which the opposite connectivities would result. *b*) The branching ratios of the reaction products formed from the respective intermediates (C$_4$H$_8$)Fe$^+$ (H,CN) reflect the presence of a HNC ligand for (*t*-Bu)NC and of HCN for (*t*-Bu)CN [30a], underlining the results from

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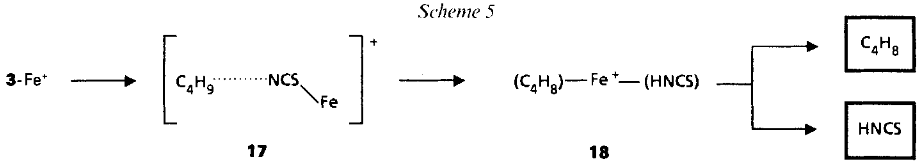
[4]) There is considerable precedent for ion/(induced) dipole complexes as intermediates in unimolecular reactions of gaseous cations. For reviews, see [28]; for criteria of their intermediacy, see [29].

point *a*. Furthermore, it could be shown that in related systems, which also gave rise to [H,CN] and $[Fe,H,CN]^+$ complexes (*e.g.* (*s*-Bu)CN–M^+ (M = Co,Ni,Cu), *t*-C_5H_{11}CN–Fe^+), *all* hydrogens participate in the product formation, not only those in the *β*-positions [30b,c], which reveals the intermediacy of *carbenium-type ions*, for which hydrogen equilibration is rapid [32].

The label distribution for the present system is considered as an indication for the operation of the ion/dipole mechanism. To substantiate this proposal, and to get further information about the structure of the $[Fe,H,N,C,S]^+$ ions, collisional activation (CA) experiments were performed, using a variety of different $C_nH_{2n+1}NCS$ and $C_nH_{2n+1}SCN$ precursors. All of them gave rise to intense signals for $[Fe,H,N,C,S]^+$ ions already in the ion source, and it was found that two distinct $[Fe,H,N,C,S]^+$ isomers were formed from thiocyanates and isothiocyanates. They could be distinguished by small, though structure-indicative, signals for FeC^+ and FeN^+ and, in addition, by differently intense $[M - H]^+$ ions. For both isomers, the CA spectra were dominated by abundant signals for Fe^+ and FeS^+ in roughly similar intensities, which accounted alone for *ca.* 90% of the total daughter-ion current. The exact structure of the isomeric complexes is still under further investigation, but it is suggested that upon collisional activation sulfur is split off, and $Fe(HNC)^+$ ions are formed from those complexes that arise from isothiocyanates. On the other hand, from the isomeric complexes, that are generated from thiocyanates, $Fe(HCN)^+$ ions are formed upon sulfur loss. These tentative interpretation is largely based upon a comparison with the authentic $M(H,CN)^+$ complexes that also can be distinguished by their respective MC^+ or MN^+ fragments [30a] [33]. Even though the exact structure of the $[Fe,H,N,C,S]^+$ ions from isothiocyanates is not yet established, it is obvious, however, that an insertion of the metal ion into the CH_2–N bond can be excluded, as this process would result in a connectivity between Fe^+ and N, which is not observed. This finding, together with the labeling results in mind, lets us, therefore, propose that the ion/dipole mechanism, depicted in *Scheme 5*, is indeed the actual pathway by which HNCS and $Fe(HNCS)^+$ are formed.

Scheme 5



Coordination of Fe^+ to the functional group induces cleavage of the CH_2–N bond, producing the ion/dipole complex **17**. As ion/dipole complexes can be stable for quite long times [28] [34], hydrogen equilibration in the incipient carbenium-ion part of **17** takes place, before the metal-containing fragment is protonated, affording **18**. This biligated intermediate **18** now dissociates according to the relative binding energies of its two ligands to the metal ion.

Loss of 27, 28, and 29 Dalton. The mechanisms that lead to the losses of [H,CN], C_2H_4 and $[H_3,N,C]$ unfortunately could not be elucidated as the limited daugther-ion resolution of the sector-field instruments did not permit a distinction of the various isobaric products that were generated from **3a**-Fe^+ to **3c**-Fe^+. *Fourier* transform ion cyclotron resonance (FTICR) experiments are currently under way that, hopefully, will permit us to answer these open questions.

Most likely, however, loss C_2H_4 occurs from intermediate **II** (*Scheme 1*, M = Fe, X = NCS) by β-CC cleavage, analogous to other systems where 'remote functionalization' is operative and where loss of ethylene always accompanies loss of H_2 [5k,m,n] [13] [16–19] [30b,c].

Ethyl Isothiocyanate and Propyl Isothiocyanate. Dehydrosulfurization represents only a minor pathway for both compounds, the main reaction being the formation of $Fe(HNCS)^+/HNCS$. It seems resonable to assume that no change in mechanism occurs and that the ion/dipole mechanism applies in these systems as well. An interesting feature can be extracted from a comparison of the branching ratios that are observed for the loss of HNCS *vs.* the respective alkenes. The retainment of the stronger bound HNCS ligand is favored over ethylene by 32:1, by 6.4:1 over propene, and by only 2.5:1 over butene. This decreasing ratios clearly reflect the increasing binding energies of higher substituted alkenes, completely in line with previous results [13b] [35].

Conclusions. – The reactions of alkyl isothiocyanates with bare gas-phase Fe^+ have been studied. Investigation of appropiately labeled compounds allows to draw the following mechanistic conclusions: dehydrosulfurization, which is first observed in high intensity for BuNCS, is due to an unique process where remote H-atoms from the ω and $(\omega - 1)$ position serve as an internal H source. Remote functionalization gives rise to molecular H_2 and probably ethylene as well, while insertion of Fe^+ into the C(2)–C(3) bond of **3**, followed by β-H shift, leads to propene formation. $Fe(HNCS)^+$ complexes and neutral HNCS are formed by a mechanism that proceeds *via* intermediate ion/dipole complexes and without insertion into the CH_2–NCS bond.

Experimental Part

Part of the experiments described here was performed using a commercially available *VG ZAB-HF-3F* mass spectrometer with a BEB configuration (B magnetic, E electric sector). The instrument [36] and the operating principles have been described earlier [13] [16–19] [30] [33]. Briefly, the simultaneous introduction of $Fe(CO)_5$ and the org. substrates into a CI source (100-eV ionizing energy, 0.5 mA emission current, 0 V repeller voltage, 470 K source temp., 10^{-5} mbar source-housing pressure) gives, among other products, rise to 1:1 adduct complexes of Fe^+ with the substrates. Those are selected in a double-focussing mode with $B_{(1)}E$ (8 kV acceleration voltage, 3000–5000 mass resolution in the 10% valley definition), and $B_{(2)}$ is scanned to monitor the unimolecular decompositions (*metastable ions* (MI), background pressure 10^{-8} mbar) occurring in the 3rd field-free region between E and $B_{(2)}$. Collisional activation is accomplished by introducing He as a stationary-target gas in a collision cell located in the focal plane of the 3rd field-free region (*ca.* $10^{-5.5}$ mbar, 80% transmission). Recently, this instrument was upgraded to a four-sector machine with a BEBE configuration, and part of the work was performed with this modified mass spectrometer. Using similar conditions, namely MI spectra in the 3rd field-free region, nearly identical spectra resulted. All spectra were handeled with the *VG 11/250* data system, and 10–50 scans were averaged to improve the signal-to-noise ratio.

Compounds were synthesized according to established procedures, purified with prep. GC and characterized by NMR and GC/MS.

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