154. Gas-Phase Chemistry of Ti$^+$ to Zn$^+$ with Butyl Isothiocyanate

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Using a complete set of ^{2}H-labeled isotopomers, the gas-phase reactions of Ti$^+$ to Zn$^+$ with butyl isothiocyanate are studied. The main product for most of the metal ions is MHNCS$^+$ formed by an ion/dipole mechanism. Exceptions are Cr$^+$, which yields significant amounts of H$_2$ and H$_2$S loss, Mn$^+$, which is the only ion that does not form MHNCS$^+$ at all but produces mainly C$_2$H$_4$ and C$_3$H$_6$, and Zn$^+$, which predominantly reacts by charge transfer.

Introduction. – Gas-phase organometallic chemistry [1] can be used to study the intrinsic properties of bare transition-metal ions. The absence of a solvent shell or counter ions simplifies the analysis and simultaneously makes the 'bare' ion more reactive towards bond activation. Nevertheless, the oxidative addition of, *e.g.*, a C–H or C–C bond may be precluded by energetic reasons so that the metal ion is either completely unreactive towards the substrate or only gives rise to adduct complexes. One other possibility the metal ion has in this case, is to react by the ion/dipole mechanism [2–6].

So far, we found this mechanism to be operative for several alkane derivatives C$_n$H$_{2n+1}$X; the bare metal ion abstracts the functional group of the substrate as an anion, and this results in the formation of a carbenium-ion/dipole complex. Simple separation to afford C$_n$H$_{2n+1}^+$ and neutral MX is in most cases endothermic, however; and thus the complex rearranges by proton transfer from the incipient carbenium ion to the metal-containing dipole yielding a mixed complex which undergoes competitive ligand loss

Scheme 1

M$^+$ + C$_n$H$_{2n+1}$X ⟶ [C$_n$H$_{2n+1}$ --- XM]$^+$ ⟶ (C$_n$H$_{2n}$)M$^+$(HX) ⟶ M(C$_n$H$_{2n}$)$^+$ / M(HX)$^+$
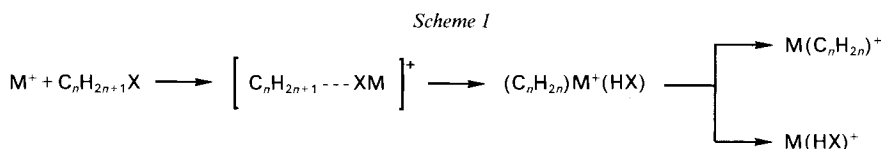
(Scheme 1). This mechanism avoids any insertion steps and is probably more prevalent than might be thought; its operation may be overlooked, because insertion of the metal ion into the C–X bond followed by β-H shift results in the same products [7].

Several criteria can be used to detect the operation of the ion/dipole mechanism. The most convincing but not always applicable way is to prove that the initial coordination site is preserved in the course of the reaction. Nitriles and isonitriles are textbook

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examples to illustrate this point; in the former case, metal ions, reacting *via* intermediate-ion/dipole complexes, will stick to the N-atom and form $HCN-M^+$ ions, while in the latter case it is the C-atom that is used for the initial coordination of RNC as well as in the $HNC-M^+$ product. Similarly, if X is a bifunctional group, like CN or NC, one coordination site is blocked by the metal ion in the carbenium-ion/dipole complex, and hence, protonation can only occur on the other coordination site. One can, thus, detract information about metal-ion coordination also from the structures of the neutral HX particles that are produced. It was possible to distinguish HCN and HNC, generated from nitriles and isonitriles, respectively, in the isomeric $(H,CN)M^+$ ions as well as in the neutral (H,CN) losses [2–6] [8]. Another criterion is based on the lifetimes of the ion/dipole complexes; being trapped on the reaction coordinate by a potential-energy barrier on one side and an entropic bottleneck on the other side [9], they are known to be quite long-living [10]. For carbenium ions, however, H-rearrangements are fast processes [11], and thus H/D scrambling in ^{2}H-labeled substrates may be expected. This prediction could be verified [3–6], although it is, of course, always possible to explain H/D scrambling assuming reversible β-H shifts and interconversion of isomeric alkyl groups *via* hydrido-alkene complexes [7].

The operation of the ion/dipole mechanism has also been assumed to account for the formation of $FeHNCS^+$ ions and losses of HNCS in reactions of Fe^+ with isothiocyanates [12]. To obtain more evidence for this contention we decided to study all first d-row transition-metal ions from Ti^+ through Zn^+ with BuNCS (**1**) and its isotopomers **1a–d** using a *Fourier*-transform ion-cyclotron resonance (FTICR) spectrometer [13]. Any
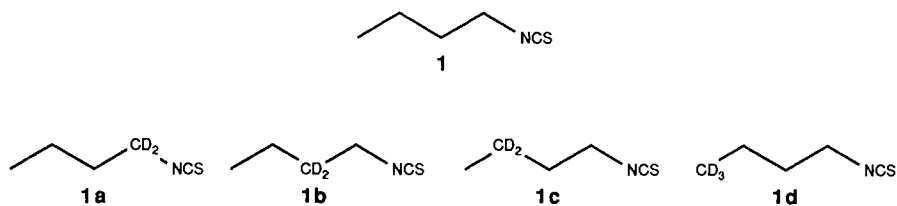
relative increase of the $MHNCS^+$ and HNCS products for metal ions unable to react by oxidative addition, *i.e.*, insertion/β-H shift, would be a further strong argument for the operation of the ion/dipole mechanism. For nitriles, a steady increase for the ion/dipole *vs.* other mechanisms was indeed found for Fe^+-Cu^+, with the d^{10} Cu^+ ion exclusively reacting *via* intermediate ion/dipole complexes [6] [14].

Results and Discussion. – The products generated in the reactions of M^+ with BuNCS are given in *Table 1*. It can be seen that except for Cr^+, Mn^+, and Zn^+, the main product is $MHNCS^+$ (*Eqn. 1*). Loss of HNCS is also observed (*Eqn. 2*), but in much smaller intensities, which is not altogether unexpected, since the branching ratio for the neutral losses from $M(C_nH_{2n})(HX)^+$ (*Scheme 1*) is determined by the binding energy of the two ligands to the metal ion.
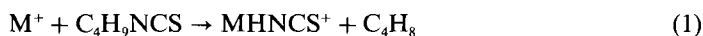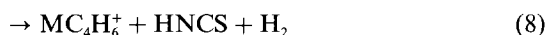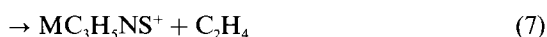
$$M^+ + C_4H_9NCS \rightarrow MHNCS^+ + C_4H_8 \qquad (1)$$

$$\rightarrow MC_4H_8^+ + HNCS \qquad (2)$$

Table 1. *Products Generated in the Reaction of M^+ with BuNCS[a])*

∧∧NCS	Ti^+	V^+	Cr^+	Mn^+	Fe^+	Co^+	Ni^+	Cu^+	Zn^+
$MHNCS^+$	68	97	28	–	75	65	78	93	12
HNCS	–	–	–	–	3	4	7	7	1
[MNCS]	7	–	–	–	3	2	–	–	–
$[C_5H_9N]$	22	–	–	–	–	–	–	–	–
$[HNC, H_2]$	3	3	–	–	–	–	–	–	–
$M(BuNCS)^+$	–	–	9	–	–	–	–	–	–
H_2	–	–	35	2	< 1	1	< 1	–	–
$2H_2$	–	–	3	–	–	–	–	–	–
H_2S	–	–	18	9	2	1	–	–	–
H_2, H_2S	–	–	2	–	–	–	–	–	–
C_3H_6	–	–	2	20	< 1	–	–	–	–
$[C_2H_4S]$	–	–	3	–	–	–	–	–	–
$[C_2H_3]$	–	–	–	13	–	–	–	–	–
C_2H_4	–	–	–	57	–	6	3	–	–
$HNCS, H_2$	–	–	–	–	13	21	11	–	–
M	–	–	–	–	–	–	–	–	87

[a]) Intensities are expressed in Σ products $= 100\%$.

HNCS is obviously much stronger bound than butene, and thus $MHNCS^+$ is the predominant product. The complete absence of HNCS loss for the early transition-metal ions Ti^+–Cr^+ is strange, however, and might point to a different mechanism for the $MHNCS^+$ formation. Thus, we will divide the discussion into groups and, for didactic reasons, will begin with Fe^+–Cu^+.

Fe^+, Co^+, Ni^+, and Cu^+ Ions. In addition to the reactions indicated in *Eqns. 1* and *2*, six other reactions are observed for these metal ions and are given in *Eqns. 3–8*. Note, however, that not all of the products are formed for each ion, respectively (*Table 1*).

$$M^+ + C_4H_9NCS \rightarrow C_4H_9^+ + [MNCS] \tag{3}$$

$$\rightarrow MC_5H_7NS^+ + H_2 \tag{4}$$

$$\rightarrow MC_5H_7N^+ + H_2S \tag{5}$$

$$\rightarrow MC_2H_3NS^+ + C_3H_6 \tag{6}$$

$$\rightarrow MC_3H_5NS^+ + C_2H_4 \tag{7}$$

$$\rightarrow MC_4H_6^+ + HNCS + H_2 \tag{8}$$
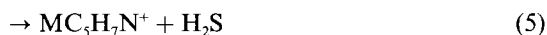
To gain more information about the mechanisms responsible for *Eqns. 1–8*, we have also studied the reactions of the ^2H-labeled compounds **1a–d** (*Table 2*). As can be seen from *Table 2*, the labeling distribution for the products from *Eqn. 1* is very similar or even identical to that from *Eqn. 2* for all metal ions and all isotopomers. Differences may arise from secondary isotope effects, the larger uncertainty in the determination of the small HNCS/DNCS loss products, or, more likely, from primary isotope effects in the subsequent decomposition of the HNCS loss products via *Eqn. 8* (see below). Thus, it can be safely concluded that the products arise from a common intermediate, such as $M(C_4H_8)(HNCS)^+$. Although neither the structure of the $MHNCS^+$ ions could be determined [12], nor could the identity of the HNCS neutrals [15] be established, the H/D

Table 2. *Products Generated from the Reactions of Fe^+–Zn^+ with Labeled Butyl Isothiocyanates*[a]

	1a					1b					1c					1d				
	Fe^+	Co^+	Ni^+	Cu^+	Zn^+	Fe^+	Co^+	Ni^+	Cu^+	Zn^+	Fe^+	Co^+	Ni^+	Cu^+	Zn^+	Fe^+	Co^+	Ni^+	Cu^+	Zn^+
$MHNCS^+$	90	89	87	86	91	78	85	79	81	78	70	78	68	71	70	90	93	90	87	92
$MDNCS^+$	10	11	13	14	9	22	15	21	19	22	30	22	32	29	30	10	7	10	13	8
HNCS	86	~82	88	89	~100	74	63	~69	78	71	65	78	68	60	56	100	82	~90	89	91
DNCS	14	~18	12	11	[b]	28	37	~31	22	29	35	22	32	40	44	[b]	18	~10	11	9
H_2	–	100	–	–	–	–	100	–	–	–	–	[c]	–	–	–	–	–	–	–	–
HD	–	–	–	–	–	–	–	–	–	–	–	[c]	–	–	–	–	100	–	–	–
H_2S	80	[c]	–	–	–	78	[c]	–	–	–	55	[c]	–	–	–	–	[c]	–	–	–
HDS	20	[c]	–	–	–	22	[c]	–	–	–	45	[c]	–	–	–	100	[c]	–	–	–
C_3H_6	100	–	–	–	–	–	–	–	–	–	100	–	–	–	–	–	–	–	–	–
C_3H_5D	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
$C_3H_4D_2$	–	–	–	–	–	100	–	–	–	–	–	–	–	–	–	–	–	–	–	–
$C_3H_3D_3$	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	100	–	–	–	–
C_2H_4	–	21	40	–	–	–	20	33	–	–	–	76	66	–	–	–	89	85	–	–
$C_2H_2D_2$	–	79	60	–	–	–	80	67	–	–	–	24	34	–	–	–	11	15	–	–
$HNCS, H_2$	65	69	67	–	–	57	54	47	–	–	50	56	50	–	–	36	38	43	–	–
$[DNCS, H_2]$	33	31	33	–	–	39	42	45	–	–	50	44	50	–	–	64	62	57	–	–
$[DNCS, HD]$	2	–	–	–	–	3	4	8	–	–	–	–	–	–	–	–	–	–	–	–

[a] Intensities are normalized to 100% for each neutral loss.
[b] Possibly too weak to be detected.
[c] Could not be determined, see text.

scrambling observed here strongly points to the operation of the ion/dipole mechanism. This is further supported by the observation that Cu^+ exclusively reacts *via Eqns. 1* and *2.* Cu^+ with its d^{10} configuration should be unable to undergo oxidative addition reactions, but as a *Lewis* acid, it can still react by the ion/dipole mechanism.

The reaction indicated in *Eqn. 3* is observed for Fe^+ and Co^+ and may be explained as arising from separation of the ion/dipole complex. Initially, we suspected the $C_4H_9^+$ product to be due to a small amount of kinetically or electronically excited metal ions present in the reagent population. To rule out this possibility, Fe^+ was subjected to extended periods of trapping time with the Ar buffer gas to quench any excess energy possibly present. Afterwards, Fe^+ was reisolated and allowed to react again; however, no change in product distribution resulted. Since this procedure was previously found to be effective to remove all excess energy [16], we, therefore, conclude that all products result from the reactions of ground-state ions.

The reaction given in *Eqn. 4* is observed to a detectable extent only for Co^+; unfortunately the labeling distribution for the H_2 loss could not be determined for **1c**, as the sample prepared had only an isotopic purity of 88%[2]), and interferences with the adduct complex of **1** with Co^+ were encountered. However, the results for the three remaining isotopomers are straightforward to interpret; one H is provided by the ω and the other by the $(\omega -1)$ position, and thus we are dealing with quite another example for 'remote functionalization' [1] [4] [18]. A transition-metal ion anchored to the functional group X of a substrate $C_nH_{2n+1}X$ activates remote C$-$H bonds by oxidative addition. For substrates with a medium chain length, this involves exclusively the terminal CH_3 group and the resulting intermediate undergoes β-H shift followed by reductive elimination of H_2. Altogether, an $\omega/(\omega -1)$-unsaturated substrate results, which now coordinates the metal ion by the C=C bond and the functional group X in a bidentate fashion. Although dehydrogenation was also present in the Fe^+ and Ni^+ systems, the intensity of these processes was below 1% so that they could not be accurately quantified because of limitations in dynamic range.

Loss of H_2S (*Eqn. 5*) is noted for Fe^+ and Co^+, but for Co^+, the labeling distribution could not be determined for intensity reasons. Dehydrosulfurization of BuNCS by Fe^+ was also noted in our previous study which used metastable-ion (MI) decompositions in a multi-sector mass spectrometer [12]. This intramolecular variant of the industrially important hydrodesulfurization (HDS) [19] was much more prominent in the MI spectra and also proceeded with a slightly different labeling distribution. The mechanism we proposed [12] is given in *Scheme 2* and commences with S abstraction, which yields a complex of FeS^+ with butyl isocyanide (**2**). Sulfur abstraction in the gas phase has been noted for Fe^+ before [20] [21] and is also well known in solution for isothiocyanates [22] as

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[2]) Compound **1c** is prepared by $LiAlD_4$ reduction of AcCl in Et_2O, evaporation of the solvent *in vacuo* to dryness, treatment of the solid residue at $-196°$ with 68% HBr, distillation of CH_3CD_2Br, and conversion of the latter to the *Grignard* reagent which is treated with CO_2 to afford $CH_3CD_2CO_2H$. The acid is reduced with $LiAlH_4$, workup with HBr and subsequent distillation affords $CH_3CD_2CH_2Br$ which is converted to $CH_3CD_2CH_2CN$ using NaCN in DMSO at $110°$. The nitrile is reduced to $CH_3CD_2(CH_2)_2NH_2$ using $LiAlH_4/H_2SO_4$ and by a procedure similar to the one given in [17]. This amine is converted to the sodium salt of the dithiocarbamic acid, $CH_3CD_2(CH_2)_2NHCS_2Na$, which is treated with $ClCO_2Et$. The reaction product is thermally decomposed to **1c**. Unfortunately, solvent evaporation in the first step was incomplete, and the remaining Et_2O afforded EtBr with the HBr, so that the final product after preparative GC consisted of *ca.* 88% **1c** and 12% **1**. For most of the neutral losses **1** did not interfere, or its abundance could be corrected for.

Scheme 2

1-Fe⁺   2   3   4   5
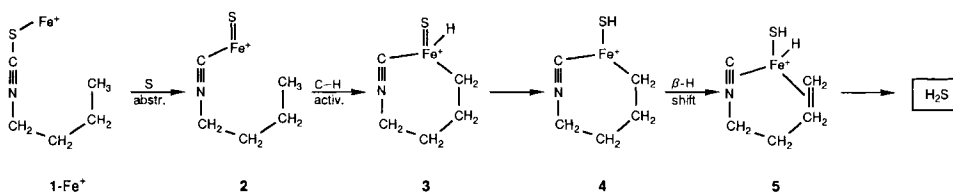
well as other substrates [22i] [23] with a proper leaving group. The following steps are analogous to the usual remote-functionalization mechanism, only that a ligated metal ion is involved. We have previously shown that the related FeO^+ is also able to react by remote functionalization [24]. In solution, it has been found that HS^- attack at coordinated isocyanides may give rise to isothiocyanate complexes [25], which would represent the reverse reaction, *i.e.*, from **4** to **1**. If the reductive elimination of H_2S from **5** is subject to an activation barrier, scrambling might occur at this stage by reversible allylic C–H activation. This would explain why **1d** exclusively affords HDS, in contrast to the other three isotopomers.

Loss of propene for Fe^+ (*Eqn. 6*) was also noted before [12], and the same labeling distribution is observed. We propose the mechanism given in *Scheme 3* which is in accord with all experimental findings. Insertion into the C(1)–C(2) bond is followed by β-H shift and rearrangement to **8**, which exclusively loses C_3H_6 as the less stronger-bound ligand.

Scheme 3

6   7   8
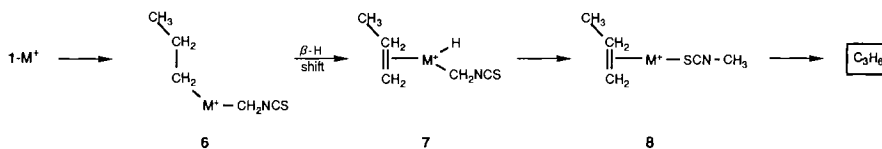
Ethene loss (*Eqn. 7*) involves exclusively intact methylene units as can be seen from the absence of C_2H_3D or C_2HD_3 losses in *Table 2*; Co^+ and Ni^+ show a similar labeling distribution of C_2H_4 and $C_2H_2D_2$ losses. We could not rationalize the results with one single mechanism as it seems that roughly 60–80% of the ethene originates from the α/β-position and the remainder from the γ/δ-position. The latter part could be formed by remote functionalization; insertion into a CH_3 bond is followed by β-C,C cleavage and ethene loss, analogous to many other substrates [1] [4] [18]. Insertion into the N–C(1) bond preceding β-C,C cleavage could account for the major portion of the ethene that is produced.

As double-resonance experiments [26] show, the $MC_4H_6^+$ ions (*Eqn. 8*) are formed by loss of H_2 from $MC_4H_8^+$, thus, loss of HNCS is followed by loss of H_2 and not *vice versa*. $MC_4H_8^+$ ions, if formed with suffcient energy, are often observed to further eliminate H_2 to form stable butadiene complexes [1]. The labeling distribution in *Table 2* can be explained by assuming either interconverting butene complexes preceding dehydrogenation or reversible steps in the course of the latter process.

Table 3. *Comparison of the FTICR Results for Fe$^+$/BuNCS^a) with the MI Decompositions of [Fe(BuNCS)]$^+$ Complexes^b) in a Multi-Sector Instrument^c)*

Products	FTICR	Ml	Products	FTICR	Ml
FeHNCS$^+$	75	15	C$_2$H$_4$	< 1	13
HNCS	3	6	H$_2$S	2	35
HNCS, H$_2$	13	–	C$_3$H$_6$	< 1	4
[FeNCS]	3	–	[HNC]	< 1	7
H$_2$	< 1	17	[C$_2$H$_5$]	< 1	2^d)

^{a}) Present study; this *Table* also includes very small products not listed in *Table 1*. An intensity of < 1% indicates that the product is observed, but its exact intensity cannot be accurately specified due to limitations in dynamic range.
^{b}) [12].
^{c}) Intensities are expressed in Σ products = 100%.
^{d}) In [12], the loss of 29 amu was incorrectly assigned to loss of [HNC, H$_2$], the much higher resolution of the FTICR reveals, however, that loss of [C$_2$H$_5$], analogous to Mn$^+$ (see below), takes place.

Differences are observed between the present results and our earlier study on Fe$^+$/ C$_4$H$_9$NCS [12] (*Table 3*). In the latter, products due to remote functionalization were much more prominent, *i.e.*, H$_2$, C$_2$H$_4$, and H$_2$S, while those of the ion/dipole mechanism were less abundant. In the present study, FeHNCS$^+$ accounts for the majority of the products, and the HNCS-loss product even decomposes further by loss of H$_2$. As in the FTICR approach, bare Fe$^+$ ions are reacted with the substrate **1** while in the sector approach metastable decompositions of Fe(**1**)$^+$ adduct complexes are monitored, differences between the two methods may not be unreasonable. However, comparisons have so far not revealed any great differences but instead showed good or fair agreement [6] [16] [27] [28]. The suppression of the 'remote-functionalization products' in favor of the 'ion/dipole products' together with the appearance of high-energy products (HNCS/H$_2$ and C$_4$H$_9^+$) found here could, thus, be an indication that MI spectra are sampling slightly 'cooler' products. The drastic shift for Fe$^+$/**1** shows that this system represents a border-line case where small differences in energy can greatly influence the mechanism.

Zn$^+$ Ion. Zn$^+$ mainly undergoes charge transfer with BuNCS (*Eqn. 9*), in line with the ionization potential of Zn (9.394 eV) [29] as compared to **1** (9.02 eV) [30]. Part of the **1**$^+$ ions decompose further by loss of H$^\cdot$, CH$_3^\cdot$, SH$^\cdot$, and others, but this is also expected from the difference in the ionization potentials and will not be discussed further. The number given in *Table 1* includes **1**$^+$ as well as its decomposition products.

$$Zn^+ + C_4H_9NCS \rightarrow C_4H_9NCS^+ + Zn \qquad (9)$$
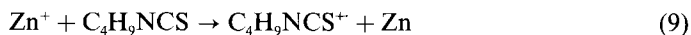
Aside from the charge transfer, only ZnHNCS$^+$ and HNCS are noted, and the labeling distribution in *Table 2* shows no differences to Fe$^+$–Cu$^+$. Zn$^+$ is also not expected to undergo oxidative addition with its d^{10}s^1 ground state, and so the exclusive formation of the products from the ion/dipole mechanism is a further strong argument against an insertion/β-H shift mechanism.

Ti$^+$ and V$^+$ Ions. Ti$^+$ and V$^+$ react as indicated in *Eqns. 1, 3* and further *10* and *11*.

$$M^+ + C_4H_9NCS \rightarrow MS^+ + C_5H_9N \qquad (10)$$
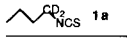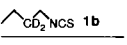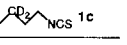
$$\rightarrow MC_4H_6S^+ + [HNC, H_2] \qquad (11)$$
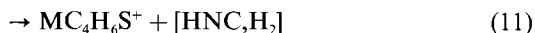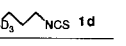
Table 4. *Products Generated in the Reactions of* Ti^+ *and* V^+ *with Labeled Butyl Isothiocyanates*[a]

	NCS 1a		NCS 1b		NCS 1c		NCS 1d	
	Ti^+	V^+	Ti^+	V^+	Ti^+	V^+	Ti^+	V^+
$MHNCS^+$	88	89	77	79	70	70	89	94
$MDNCS^+$	12	11	23	21	30	30	11	6
$[HNC, H_2]$	67	57	55	62	36	39	44	33
$[DNC, H_2]$	33	43	45	38	48	61	56	52
$[DNC, HD]$	–	–	–	–	16	–	–	14

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

The labeling distribution for *Eqns. 1* and *11* is given in *Table 4*. As noted above, loss of HNCS is completely absent which might be a hint to a different mechanism than the one in *Scheme 1*. However, in the absence of further evidence, we are reluctant to suggest a new one, in particular as the ion/dipole mechanism may well apply, *viz*, if the binding energy of HNCS would be much higher than that of butene. In that case, its loss could be completely suppressed. The formation of TiS^+ in *Eqn. 10* already points to a higher Ti-S bond strength, and V^+ and Ti^+ are also known to form MS^+ ions with ethylene sulfide [21] or ethanethiol [31]. The formation of $MC_4H_6S^+$ ions by loss of $[H_3,N,C]$ could, thus, be explained by initial S abstraction, loss of HNC from the resulting MS^+/C_4H_9NC complex *via* the ion/dipole mechanism, and subsequent dehydrogenation analogous to *Eqn. 8*. It is well known that isocyanides react easily by the ion/dipole mechanism to form HNC and $M(HNC)^+$ [2] [5] [32]. Unfortunately the intensity of the $MC_4H_6S^+$ ions was too low to perform CID experiments [33] in order to see, if indeed they possessed a $MS(C_4H_6)^+$ structure as this mechanism would imply. It can as well be speculated, if the $MHNCS^+$ ions are also formed by S abstraction and eventual formation of $MS(HNC)^+$ ions *via* the ion/dipole mechanism; this would also explain the absence of the HNCS loss.

Cr$^+$ Ion. As can be seen from *Table 1*, Cr^+ shows a completely different pattern of reactivity than the other metal ions. $CrHNCS^+$ formation according to *Eqn. 1* is observed, but is less important and has a labeling distribution different from all other metal ions (*Table 5*); the hydrogen originates mainly from C(2) with contributions from C(3) as well.

Other processes observed are loss of H_2, H_2S, C_3H_6 (*Eqns. 4–6*), and further 2 H_2, H_2/H_2S, $[C_2H_4S]$ losses as well as adduct formation (*Eqns. 12–15*).

$$Cr^+ + C_4H_9NCS \rightarrow CrC_5H_5NS^+ + 2H_2 \qquad (12)$$

$$\rightarrow CrC_5H_5N^+ + H_2 + H_2S \qquad (13)$$

$$\rightarrow CrC_3H_5N^+ + [C_2H_4S] \qquad (14)$$

$$\rightarrow CrC_5H_9NS^+ \qquad (15)$$
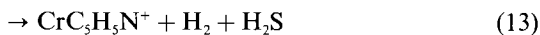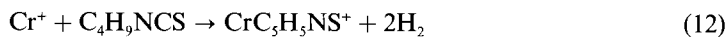
Although the adduct complex $CrC_5H_9NS^+$ is also formed in a secondary reaction from $CrHNCS^+$ (*Eqn. 16*), double-resonance experiments [26] clearly show that direct adduct formation is observed, too[3]).

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[3])   We were unable to distinguish bimolecular adduct formation from a quasi-termolecular reaction, where the $[Cr(BuNCS)]^+$ encounter complex is stabilized by a third-body collision with the Ar buffer gas.

Table 5. *Products Generated in the Reactions of Cr^+ with Labeled Isothiocyanates[a])*

	$\wedge\wedge^{CD_2}_{NCS}$ **1a**	$\wedge_{CD_2}^{}NCS$ **1b**	$\wedge^{CD_2}\wedge_{NCS}$ **1c**	$CD_3\vee\wedge_{NCS}$ **1d**
	Cr^+	Cr^+	Cr^+	Cr^+
$MHNCS^+$	100	45	60	100
$MDNCS^+$	–	55	40	–
H_2	40	70	85	62
HD	60	30	15	38
H_2S	36	70	86	37
HDS	64	30	14	63
C_3H_6	100	–	–	–
C_3H_5D	–	–	100	–
$C_3H_4D_2$	–	100	–	–
$C_3H_3D_3$	–	–	–	100
$[C_2H_4S]$	33	–	52	–
$[C_2H_3DS]$	67	46	48	54
$[C_2H_2D_2S]$	–	54	–	–
$[C_2HD_3S]$	–	–	–	46

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

$$CrHNCS^+ + C_4H_9NCS \rightarrow CrC_5H_9NS^+ + HNCS \qquad (16)$$

Unfortunately, the intensity of the double dehydrogenation product in *Eqn. 12* was too low to allow the unambiguous determination of the labeling distribution, but it is clear from the data of the single dehydrogenation in *Table 5* that all positions contribute to the H_2 losses, with the α-position being slightly favored over the others.

Dehydrosulfurization according to *Eqn. 5* is very abundant for Cr^+, yet the labeling data differs from that of Fe^+ in *Table 2* in that the major hydrogen contributions come from C(1) and C(4)! As there are also contributions from C(2) and C(3), we are unable to provide a mechanism that would account for this highly unusual loss. The loss of H_2/H_2S in *Eqn. 13* was similarly not intense enough for a determination of the labeling distribution, but it was nevertheless possible to establish the sequence in which the two neutrals were lost. While ejection [26] of $CrC_5H_7N^+$ did not influence the $CrC_5H_5N^+$ product, irradiation of $CrC_5H_7NS^+$ did, thus H_2 loss precedes H_2S loss and not *vice versa*. As the dehydrogenation is already unspecific, it is reasonable to assume that the hydrogens for the subsequent H_2S loss also arise from all positions of the substrate.

Most unusual is the loss of $[C_2H_4S]$ in *Eqn. 14*; the identity of the neutral is unknown, and many combinations are conceivable, *e.g.*, ethylene sulfide, C_2H_4/S, CH_4/CS, C_2H_2/H_2S. The labeling data in *Table 5* does not help in the distinction or in the determination of the mechanism that leads to this product. The only reaction that proceeds highly specific in the Cr^+/C_4H_9NCS systems is the propene loss which follows the same mechanism as in case of Fe^+. *Scheme 3* is in complete accordance with the labeling data in *Table 5*.

Mn⁺ Ion. Products observed for Mn^+ are H_2, H_2S, C_3H_6, C_2H_4, and $[C_2H_5^.]$, *Eqns. 4–7* and *17*. Notable is further the complete absence of $MnHNCS^+$.

$$Mn^+ + C_4H_9NCS \rightarrow MnC_3H_4NS^+ + [C_2H_5^.] \qquad (17)$$

Table 6. *Products Generated in the Reactions of* Mn^+ *with Labeled Butyl Isothiocyanates*[a])

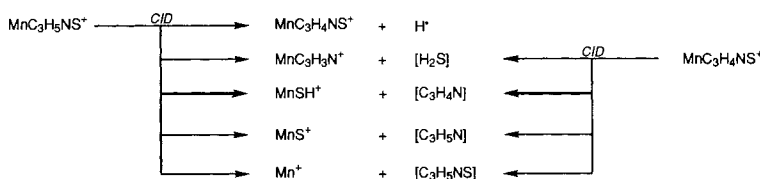|	$\diagup\!\!\diagdown\!\!\overset{CD_2}{\diagup}_{NCS}$ **1a**	$\diagdown\!\!\overset{}{C\!D_2}\!\!\diagdown_{NCS}$ **1b**	$\overset{CD_3}{\diagup}\!\!\diagdown_{NCS}$ **1c**	$_{CD_3}\!\!\diagdown\!\!\diagup\!\!\diagdown_{NCS}$ **1d**
	Mn^-	Mn^-	Mn^-	Mn^-
H_2	61	76	78	55
HD	39	24	22	45
H_2S	37	89	82	6
HDS	63	11	18	94
C_2H_4	–	–	100	100
$C_2H_2D_2$	100	100	–	–
C_3H_6	100	–	–	–
C_3H_5D	–	2	87	–
$C_3H_4D_2$	–	98	13	–
$C_3H_3D_3$	–	–	–	100
$[C_2H_5^{\cdot}]$	–	50	68	–
$[C_2H_4D^{\cdot}]$	–	–	–	37
$[C_2H_3D_2^{\cdot}]$	100	50	32	63

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

Loss of H_2, as for Cr^+, involves all positions, and the same applies for the loss of H_2S (*Table 6*). Here as well, the main hydrogen contributions come from C(1) and C(4), so obviously the same mechanism has to apply for Cr^+ and Mn^+. Propene is formed by the mechanism shown in *Scheme 3*, although some minor exchange between the β- and γ-position is noted for Mn^+. It is, however, possible that these small amounts of scrambling were much too weak in intensity to be noted for Cr^+ and Fe^+. As propene loss in case of Mn^+ accounts for 20% of the products formed, minor isotopomeric losses are more easily detected.

The loss of C_2H_4 is highly specific and exclusively involves the α - and β-CH_2 groups, thus the same mechanism probably applies that was responsible for the majority of the ethene produced by Co^+ and Ni^+. Insertion into the $N-C(1)$ bond followed by β-C,C cleavage explains the results for **1a–d** in *Table 6*. Insertion into the $C(2)-C(3)$ bond with subsequent β-C,N cleavage is considered less likely as the C,N cleavage would have to compete with β-H shift from C(4) which eventually would result in loss of C_2H_4 from the γ/δ-position.

The neutral product in *Eqn. 17* could be either $C_2H_5^{\cdot}$ or $C_2H_4/H^{\cdot}$; in the latter case one could expect that a $H^{\cdot}$ radical was lost from the $MnC_3H_5NS^+$ product in *Eqn. 7*. The labeling data in *Table 6* is, however, clearly at odds with this assumption and shows that the $[C_2H_5^{\cdot}]$ loss arises *via* a different mechanism than the ethene loss. We tried to shed more light onto this question by performimg CID experiments [33] with $MnC_3H_5NS^+$ and $MnC_3H_4NS^+$. The result is depicted in *Scheme 4* which shows that both ions form the same products with similar intensities. In particular, $MnC_3H_5NS^+$ does lose a H-atom to form $MnC_3H_4NS^+$. $MnSH^+$ is the main product for both ions; besides, Mn^+, MnS^+, and $MnC_3H_3N^+$ are formed. The latter arises by $HS^{\cdot}$ loss from $MnC_3H_4NS^+$ and, by analogy, probably by $H^{\cdot}/HS^{\cdot}$ loss from $MnC_3H_5NS^+$. Based on the CID spectra, a tentative structure for $MnC_3H_4NS^+$ could be $Mn(SH)(CN-CH=CH_2)^+$. Unfortunately, the data

Scheme 4

$$MnC_3H_5NS^+ \xrightarrow{\text{CID}}$$

$MnC_3H_4NS^+$	+	$H^{\cdot}$
$MnC_3H_3N^+$	+	$[H_2S]$
$MnSH^+$	+	$[C_3H_4N]$
MnS^+	+	$[C_3H_5N]$
Mn^+	+	$[C_3H_5NS]$

$$\xleftarrow{\text{CID}} MnC_3H_4NS^+$$

given in *Table 6* together with the seemingly conflicting CID results in *Scheme 4* did not allow us to postulate a mechanism for this unusual *radical* loss.

Conclusions. – The reactions of Ti^+–Zn^+ with BuNCS (**1**) have been studued in an FTICR instrument. Fe^+–Cu^+ react mainly *via* an ion/dipole mechanism to form $MHNCS^+$ ions or $MC_4H_8^+$ or $MC_4H_6^+$ by loss of HNCS or $HNCS/H_2$. Comparison of the FTICR results for Fe^+ with metastable decompositions of $Fe(\mathbf{1})^+$ complexes show that the product distribution for this particular system is very dependent on small changes in energy. In line with the ionization potentials, Zn^+ undergoes mainly charge transfer but except from that reacts only by the ion/dipole mechanism to form $ZnHNCS^+$ and HNCS. For Ti^+ and V^+, the main products are also $MHNCS^+$ ions, but HNCS loss is absent, and other small products are observed, too. For Cr^+ dehydrogenation dominates besides H_2S loss and $CrHNCS^+$ formation. Mn^+ does not react by the ion/dipole mechanism but mainly undergoes loss of ethene from the α/β-position and propene from $C(2)$–$C(4)$ by insertion/β-H-shift processes.

Experimental. – The experiments were performed by using a *Spectrospin CMS 47X Fourier*-transform ion-cyclotron-resonance (FTICR) mass spectrometer which is equipped with an external ion source [34]; the instrument and further details of its operation have been described in [6] [27] [35]. Briefly, metal ions were generated by laser desorption/ionization [36] by focussing the beam of a *Nd:YAG* laser (*Spectron Systems*, 1064 nm) onto a high-purity rod of the desired transition metal, which is affixed in the external ion source. The ions are extracted from the source and transferred into the analyzer cell by a system of electrostatic potentials and lenses. The ion source, transfer system, and ICR cell are differentially pumped by three turbomolecular pumps (*Balzers TPU 330* for source and cell and *Balzers TPU 50* in the middle of the transfer system). After deceleration, the ions are trapped in the field of the superconducting magnet (*Oxford Instruments*), which has a maximum field strength of 7.05 T. The metal's most abundant isotope is isolated by using FERETS [37] and allowed to react with the substrate, which is present with a constant pressure of $(1–3)\cdot 10^{-8}$ mbar; reaction times are typically 1–10 s. For collisional cooling of any excited states possibly formed and removal of kinetic energy remaining from the transfer, as well as for CID experiments [33], Ar was present as a buffer gas with a constant pressure of $(1–5)\cdot 10^{-7}$ mbar, as measured with an uncalibrated ionization gauge (*Balzers IMG 070*). All functions of the instrument were controlled by a *Bruker Aspect 3000* minicomputer; broad-band spectra were recorded with a fast *ADC*, digitized as 64-K or 128-K data points and zero-filled [38] to 256 K before *Fourier* transformation. Reaction products were unambiguously identified by high-resolution spectra and mass analysis, and their formation pathways by double-resonance and MS/MS techniques [26].

The isothiocyanates were synthesized and fully characterized using established procedures, purified by prep. GC and carefully degassed by multiple freeze-pump-thaw cycles immediately before the experiments. The label content was determined with NMR and MS techniques.

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