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Gas-Phase Reactions of Secondary and Tertiary Isocyanates with Ti^+ to Zn^+: Model Studies for Catalytic Processes

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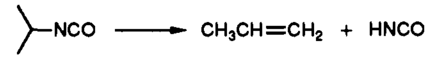
Abstract: The reactions of the first-row transition-metal ions from Ti^+ to Zn^+ with several secondary and tertiary isocyanates are studied using a Fourier transform ion cyclotron resonance (FTICR) spectrometer. The late transition-metal ions Cr^+–Zn^+ react with *i*-PrNCO (**1**), *s*-BuNCO (**2**), *t*-BuNCO (**3**), and *t*-PentNCO (**4**) via an ion/dipole mechanism to form mainly $M(HNCO)^+$ and $M(alkene)^+$ by loss of an alkene or HNCO, respectively. In contrast, the early transition-metal ions Ti^+ and V^+ show a pronouncedly different behavior. Among a plethora of small products, the most prominent pathways in the case of the secondary isocyanates **1** and **2** afford nitrile complexes by initial decarbonylation and subsequent 1,1-elimination of an alkane. For tertiary isocyanates this process is absent, revealing an inability to break two C–C bonds in the course of the alkane elimination. The results are discussed in connection with a surface-catalyzed process that generates acetonitrile from **1** and HNCO/isobutene from **3**. Some secondary reactions of Cr^+–Zn^+ are also presented. While for $M^+ = Cr^+$, Mn^+, and Zn^+ the primary $M(HNCO)^+$ and $M(alkene)^+$ products react with the secondary isocyanates to form $M(RNCO)^+$ adduct complexes by simple ligand exchange, for Fe^+–Cu^+ isomeric $M(HNCO)(alkene)^+$ ions are obtained. In the case of tertiary isocyanates, Cr^+ behaves like Fe^+–Cu^+ and only Mn^+ and Zn^+ react by simple ligand exchange.

Introduction

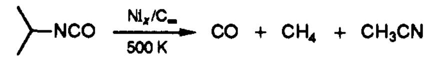
Bridging the gap between heterogeneously catalyzed processes[1] and "academic" studies performed in order to model them is still a challenge.[2] On one hand there are more or less empirically developed catalysts which are in constant contact to educts, products, and all the side products that are formed in ppm to percent amounts. On the other hand there are, for instance, well-defined single-crystal surfaces under ultra-high-vacuum conditions that are exposed to small doses of a substrate,[3] transition-metal clusters, cluster ions,[4] or even single, bare or ligated, transition-metal ions[5] that react with model substrates in high vacuum, or metal atoms embedded together with the substrate in a matrix at very low temperatures.[6] There is nevertheless a growing understanding for the mechanisms that are active on the surface of the catalysts.

In this contribution we will try to show how isolated ("bare") transition-metal ions might help to define the conditions to be met in order to develop a catalyst for a particular reaction. The reason for choosing a specific reaction was that we felt there was a lack of gas-phase studies that had a direct relationship to condensed-phase processes. Therefore we picked up a system that has been studied in more detail by Bock and Breuer,[7] namely the catalytic decompositions of alkyl isocyanates. Isopropyl isocyanate (*i*-PrNCO, **1**) can be pyrolized at 920 K to afford exclusively propene and isocyanic acid, HNCO (eq 1). In contrast, Ni_x clusters on a carbon support (Ni_x/C_∞) at 500 K are able to catalyze the decomposition of **1** yielding carbon monoxide, methane, and acetonitrile as the main products (eq 2).



(1)

1

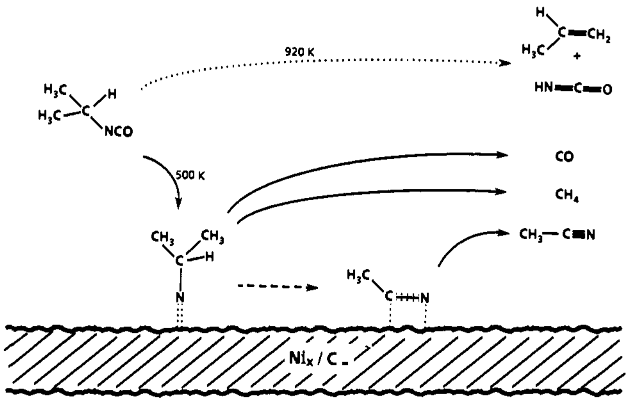


(2)

1

Since CO is formed already at 400 K, the assumption of an intermediate, surface-bound nitrene seems justified. At 500 K this nitrene undergoes CH_4 elimination and produces the thermodynamically favorable acetonitrile, which desorbs at a still slightly higher temperature. The experimental findings of Bock and Breuer are summarized in Scheme I. The uncatalyzed decomposition of *tert*-butyl isocyanate (*t*-BuNCO) requires 900 K and affords isobutene and HNCO in analogy to eq 1. Using the carbon-supported nickel catalyst, these products are already formed at 500 K, and so are NH_3 and N_2.[7a] The latter are believed to arise from disproportionation of NH species bound to the surface.

Scheme I. Schematic Representation of the Ni_x/C_∞-Catalyzed and Uncatalyzed Decomposition of *i*-PrNCO (**1**) to CO, CH_4, and CH_3CN via the Isopropylnitrene or to C_3H_6 and HNCO, respectively[a]



[a] Adopted from ref 7a.

[†] Present address: Department of Chemistry, Yale University, 225 Prospect Street, New Haven, CT 06511.

(1) E.g.: Kemball, C. *Chem. Soc. Rev.* **1984**, *13*, 375.

(2) (a) Muetterties, E. L. *Chem Soc. Rev.* **1982**, *11*, 283. (b) Garin, F.; Maire, G. *Acc. Chem. Res.* **1989**, *22*, 100.

(3) See for example: (a) Somorjai, G. A. *Chem. Soc. Rev.* **1984**, *13*, 321. (b) Somorjai, G. A. *J. Phys. Chem.* **1990**, *94*, 1013 and references cited therein. (c) Friend, C. M.; Xu, X. *Annu. Rev. Phys. Chem.* **1991**, *42*, 251.

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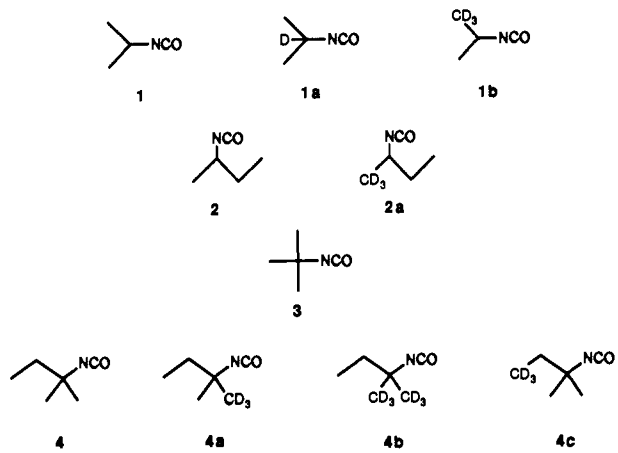
Chart I



The reactions described are interesting in several aspects. They not only provide examples of well-studied reactions in the absence or presence of a catalyst but also illustrate an obvious difference between secondary and tertiary isocyanates. The former are able to produce alkanes in a formal 1,1-elimination from the transient nitrene species while the latter are unable to do so. No C_2H_6 is observed from *t*-BuNCO, so if *tert*-butylnitrene is formed at all, its decomposition to isobutene and NH is favored over ethane elimination.

In order to examine these differences and to learn more about the mechanisms as well as the requirements for nitrile formation, we studied several alkyl isocyanates with the first-row transition-metal ions from Ti^+ to Zn^+.[8] We included **1** and its next higher homologue *sec*-butyl isocyanate (*s*-BuNCO, **2**) as examples for secondary isocyanates as well as *t*-BuNCO (**3**) with its homologue *tert*-pentyl isocyanate (*t*-PentNCO, **4**) as representative tertiary isocyanates. In particular, **2** allows us to examine if it is the stability of CH_4 that fuels the reaction in eq 2 or if C_2H_6 may be formed as well. In that case the difference between **1** and **3** would be due to the fact that two carbon–carbon bonds would have to be cleaved to generate acetonitrile. More detailed insight into the mechanisms is gained from the study of the ^{2}H-labeled isotopomers **1a**,**b**, **2a**, and **4a**–**c** (Chart I).

Experimental Section

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;[9] the instrument and further details of its operation have been previously described.[10] To this end, metal ions were generated by laser desorption/ionization[11] by focussing the beam of a Nd:YAG laser (Spectron Systems, 1064 nm) onto a high-purity rod of the desired transition metal which was 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, respectively, 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 was isolated by using FERETS[12] and allowed to react with the substrate that was present with a constant pressure of (1–3) × 10^{-8} mbar; reaction times are typically 1–10 s. For collisional cooling of excited states possibly formed, removal of kinetic energy remaining from the transfer, and collision-induced decomposition (CID) experiments,[13] argon was present as a buffer gas with a constant pressure of (1–5) × 10^{-7} mbar, as measured with an uncalibrated ionization gauge (Balzers IMG 070). All functions of the instrument are controlled by a Bruker Aspect 3000 minicomputer; broad-band spectra are recorded with a fast ADC, digitized as 64K or 128K data points and zero filled[14] to 256K before Fourier transformation. Reaction products were unambiguously identified with high-resolution spectra and mass analysis and their formation pathways by double-resonance and MS/MS techniques.[15]

Table I. Products that Arise from the Reaction of Cr^+–Zn^+ with *i*-PrNCO (**1**)[a] and Kinetic Isotope Effects Observed for $CD_3(CH_3)CHNCO$ (**1b**)

i-PrNCO	$M(HNCO)^+$	$M(C_3H_6)^+$	k_H/k_D
Cr^+	95	5	1.5 ± 0.1
Mn^+	89	11	1.5 ± 0.1
Fe^+	81	19	1.6 ± 0.1
Co^+	91	9	1.3 ± 0.1
Ni^+	95	5	1.5 ± 0.1
Cu^+	95	5	1.6 ± 0.1
Zn^+	82	18	1.2 ± 0.1

[a] Intensities are given in $\sum$ products = 100%.

The isocyanates were synthesized and fully characterized using established procedures, purified by preparative gas chromatography, and carefully degassed by multiple freeze–pump–thaw cycles immediately before the experiments. The label content was determined with NMR and mass spectrometry techniques.

Results and Discussion

The primary reactions observed for the different isocyanates will be presented in turn and afterwards compared to each other and the condensed-phase studies. Finally, we will discuss some out of the numerous secondary and higher-order reactions that are of special relevance in a different context.

Isopropyl Isocyanate. There is a clear distinction between the two early transition-metal ions Ti^+ and V^+ and the remaining first-row ions Cr^+–Zn^+. The latter react with **1** exclusively via eqs 3 and 4 (Table I). All of them afford $M(HNCO)^+$ and

$$M^+ + i\text{-PrNCO} \rightarrow M(HNCO)^+ + C_3H_6 \quad (3)$$

$$\rightarrow M(C_3H_6)^+ + HNCO \quad (4)$$

$M(C_3H_5D)^+$ upon reaction with $(CH_3)_2CDNCO$ (**1a**) and thus prove that the methyl groups exclusively are providing the hydrogen atom for the formation of HNCO (eqs 5 and 6). This

$$M^+ + (CH_3)_2CDNCO \rightarrow M(HNCO)^+ + C_3H_5D \quad (5)$$

$$\rightarrow M(C_3H_5D)^+ + HNCO \quad (6)$$

is the necessary condition so that $CD_3(CH_3)CHNCO$ (**1b**) can be used to derive intramolecular kinetic isotope effects (KIEs) for eqs 3 and 4. Experimentally we find that for all ions (Cr^+–Zn^+) practically the same KIE is operative for eqs 3 and 4, respectively, i.e. $M(HNCO)^+/M(DNCO)^+ = M(C_3H_3D_3)^+/M(C_3H_4D_2)^+ \approx 1.5$ (Table I). The identical KIE for eqs 3 and 4 shows that both product ions are formed from a common intermediate with a $[M(HNCO)(C_3H_6)^+]^*$ structure.

Two conceivable mechanisms are particularly attractive to explain the formation of this intermediate. The first possibility

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(8) Part of this work concerning **1** has already been communicated: (a) Eller, K.; Schwarz, H. *Inorg. Chem.* **1990**, *29*, 3250. (b) Eller, K.; Schwarz, H. *Ber. Bunsenges. Phys. Chem.* **1990**, *94*, 1339. (c) Eller, K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *108*, 87.

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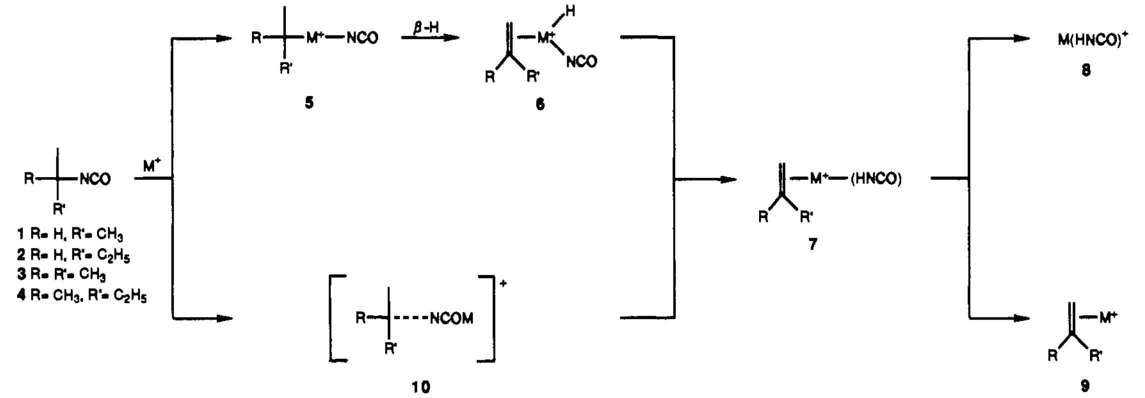
(14) (a) Horlick, G.; Yuen, W. K. *Anal. Chem.* **1976**, *48*, 1643. (b) Comisarow, M. B.; Melka, J. D. *Anal. Chem.* **1979**, *51*, 2198. (c) Giancaspro, C.; Comisarow, M. B. *Appl. Spectrosc.* **1983**, *37*, 153.

(15) (a) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413. (b) McIver, R. T., Jr.; Bowers, W. D. In *Tandem Mass Spectrometry*; McLafferty, F. W., Ed.; Wiley-Interscience: New York, 1983; p 287.

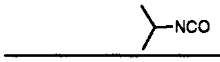
Scheme II. Formation of M(HNCO)$^+$ Products and HNCO from Alkyl Isocyanates via an Insertion/β-Hydrogen Shift or an Ion/Dipole Mechanism



is the insertion/β-hydrogen shift mechanism.[16] Insertion of the metal ion into the C–NCO bond generates **5** (Scheme II) which undergoes β-hydrogen shift to form **6** which may subsequently rearrange to afford **7**. Competitive ligand loss from **7** is in line with the identical KIEs observed in the case of **1b**. An alternative path to **7** is by way of the ion/dipole mechanism.[10a,c,17,18] Coordination of M$^+$ to the NCO group induces cleavage of the C–NCO bond and the ion/dipole complex **10** is formed. Proton transfer from the incipient carbenium ion therein to the nitrogen atom of the metal-containing dipole[19] furnishes **7** which dissociates as described above.

The two mechanisms are indistinguishable on the basis of the data for **1**. In other systems, where the ion/dipole mechanism was found to be active,[10a,c,17,20] one criterium that indicated its operation was hydrogen scrambling. Being trapped on the reaction coordinate by a potential-energy barrier on one side and an entropic bottleneck on the other side,[18] ion/dipole complexes are known to be quite long-lived sometimes.[21] On the contrary, hydrogen rearrangements in carbenium ions are fast processes,[22] so that H/D scrambling in **10** could be expected. Unfortunately, it is already known from other studies, in which a 2-propyl cation is generated as constituent of an ion/dipole complex of not too high energy, that scrambling is negligible and exclusively the CH$_3$ groups provides a hydrogen atom.[18,23,24] The absence of H/D scrambling in **1a** and **1b** therefore cannot be taken as evidence against the ion/dipole mechanism. The results for the other isocyanates presented below also do not allow a *rigorous* distinction between the two mechanisms so that we have to conclude that the ambiguity of the mechanism cannot be settled at present. There are, however, some indications for the operation of the ion/dipole mechanism, and for this reason as well as for convenience we will discuss the other examples in terms of this mechanism, but we would like to point out that they may almost equally well be described with insertion/β-H shift sequences.

Table II. Products that Arise from the Reaction of Ti$^+$ and V$^+$ with *i*-PrNCO (**1**)[a]

 NCO	Ti$^+$	V$^+$
M(HNCO)$^+$	30	17
HNCO	3	<1
CO, CH$_4$	57	74
CO, H$_2$	5	4
CO		≪1
[C$_4$H$_6$O]	5	3
[C$_4$H$_7$N]	?	1

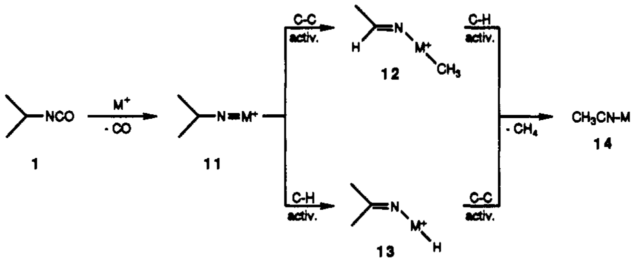
[a] Intensities are given in $\sum$ products = 100%.

Table III. Products that Arise from the Reaction of Ti$^+$ and V$^+$ with (CH$_3$)$_2$CDNCO (**1a**) and CD$_3$(CH$_3$)CHNCO (**1b**)[a]

	Ti$^+$		V$^+$	
reaction products	(CH$_3$)$_2$-CDNCO	CD$_3$(CH$_3$)-CHNCO	(CH$_3$)$_2$-CDNCO	CD$_3$(CH$_3$)-CHNCO
CH$_3$CN–M$^+$	100	41	100	42
CD$_3$CN–M$^+$		59		58
M(HNCO)$^+$	100	57	100	62
M(DNCO)$^+$		43		38
CO, H$_2$	12	69	65	67
CO, HD	88	31	35	33

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

Scheme III. Formation of Acetonitrile Complexes in the Reactions of Ti$^+$ and V$^+$ with *i*-PrNCO (**1**)



In distinct contrast to Cr$^+$–Zn$^+$ are the reactions of Ti$^+$ and V$^+$ with *i*-PrNCO (Table II). Although M(HNCO)$^+$ formation

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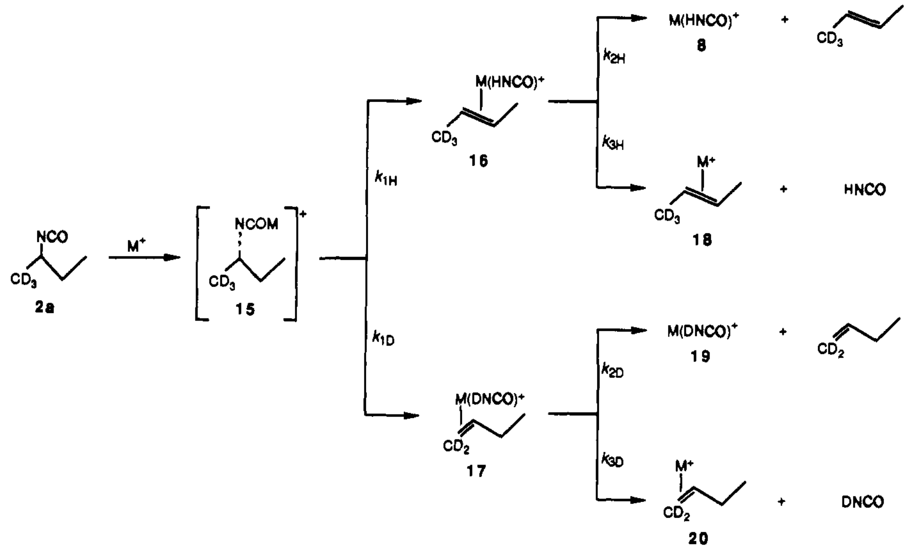
Scheme IV. Reaction of M^+ with $C_2H_5CH(CD_3)NCO$ (**2a**) To Form $M(HNCO)^+$, $M(DNCO)^+$, HNCO, and DNCO, Demonstrating That Four Different Processes Are Involved



as well as loss of HNCO are still observed, these processes are greatly diminished in importance, and the main product in both cases is $MC_2H_3N^+$ (eq 7). Both ions also form $MC_3H_5N^+$ by

$$M^+ + i\text{-PrNCO} \rightarrow MC_2H_3N^+ + [CO, CH_4] \quad (7)$$

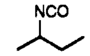
loss of [CO, H_2], and MNH^+ as well as MO^+ ions are observed. The metal oxide cations cannot, however, unambiguously be related to a reaction with **1**. The ever-present background water or other oxygen-containing impurities in the vacuum manifold are in fact even more likely the precursors for these products. At least for Ti^+ this was evidenced by day-to-day fluctuations observed for TiO^+.

Collision-induced dissociation (CID)[13] of $TiC_2H_3N^+$ showed only loss of the complete ligand and concomitant formation of Ti^+; for $VC_2H_3N^+$, at the highest energies accessible, weak signals for losses of $CH_3^\bullet$, $CN^\bullet$, and HCN in addition to the main product V^+ were observed. The spectra are therefore in line with the assumption of an acetonitrile ligand, respectively. This contention is also supported by the results for the labeled substrates **1a** and **1b** given in Table III. With the exception of the CO/H_2 loss in the case of **1a**, a very similar labeling distribution is found for Ti^+ and V^+, indicating that the same mechanisms are operative. The $MC_2H_3N^+$ formation is rationalized in Scheme III.

The first step most likely proceeds via loss of CO and produces the nitrene complex **11** in which either a C–C or a C–H bond can be activated. Further rearrangement of **12** by C–H or **13** by C–C activation is followed by reductive elimination of CH_4 and yields the observed acetonitrile complexes **14**. Which of the two conceivable pathways the reaction actually follows cannot be determined. Although observation of combined CO/H_2 loss might point to initial C–H activation, the different label distribution shows that this process is more complicated and does not necessarily proceed via **13**.

The mechanism in Scheme III is supported by the following points: Firstly, albeit with extremely low intensity, for V^+, loss of CO is observed as well, thus demonstrating the principle feasibility of this step. Yet, the structure of this $VC_3H_7N^+$ ion could not be further probed by CID and ejection experiments were inconclusive; no change in product distribution could be observed, probably due to the fact that further decomposition of this intermediate is more rapid than the ejection sequence. Secondly, the absence of any scrambled products speaks against involvement of the methyl C–H bonds and clearly proves the formal presence of a 1,1-elimination. Finally, nitrenes such as **11** are also common intermediates in the condensed-phase chemistry of isocyanates reacting with transition-metal complexes[25-27] and in the surface-catalyzed process (Scheme I).[7]

Table IV. Products that Arise from the Reaction of Ti^+–Zn^+ with *sec*-Butyl Isocyanate (**2**)[a]

	Ti^+	V^+	Cr^+	Mn^+	Fe^+	Co^+	Ni^+	Cu^+	Zn^+
$M(HNCO)^+$	30	5	90	80	55	87	85	95	38
HNCO			10	20	20	5	5	5	26
HNCO, H_2		3			25	8	4		
[MNCO]	8						6		36
CO, CH_4	16	8							
CO, C_2H_6	19	72							
CO, H_2		10							
CO, $2H_2$	20								
CO, CH_4, H_2	1								
[C_2H_6]	1								
[C_5H_8O]	5								
[C_5H_9N]	*b*	1							

[a] Intensities are given in $\sum$ products = 100%. [b] Present in significant amounts (≈20% of the total ions) but probably due to reaction of Ti^+ with H_2O. See discussion for **1**.

***sec*-Butyl Isocyanate.** The products that are formed from *s*-BuNCO (**2**) and Ti^+–Zn^+ are given in Table IV. We will again defer the discussion of Ti^+ and V^+ until the late transition-metal ions have been described; a glance at Table IV reveals that they exhibit a completely different pattern of reactivity.

All of the metal ions from Cr^+ to Zn^+ react with **2** to produce HNCO and $M(HNCO)^+$ in analogy to eqs 3 and 4. Two further products are occasionally observed, namely $C_4H_9^+$ by loss of

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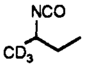
(25) Cenini, S.; La Monica, G. *Inorg. Chim. Acta* **1976**, *18*, 279.

(26) Braunstein, P.; Nobel, D. *Chem. Rev.* **1989**, *89*, 1927.

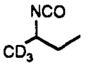
(27) E.g.: (a) Kolomnikov, I. S.; Koreshkov, Y. D.; Lobeeva, T. S.; Volpin, M. E. *J. Chem. Soc., Chem. Commun.* **1970**, 1432. (b) Kolomnikov, I. S.; Koreshkov, D.; Lobeeva, T. S.; Vol'pin, M. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 2065; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1971**, 1951. (c) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2651. (d) Tooze, R. P.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 2711. (e) Green, M. L. H.; Moynihan, K. J. *Polyhedron* **1986**, *5*, 921. (f) Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826. (g) Ehrenfeld, D.; Kress, J.; Moore, B. D.; Osborn, J. A.; Schoettel, G. *J. Chem. Soc., Chem. Commun.* **1987**, 129. (h) Su, F.-M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron* **1989**, *8* 1261. (i) Schoettel, G.; Kress, J.; Osborne, J. A. *J. Chem. Soc., Chem. Commun.* **1989**, 1062. (j) Herrmann, W. A.; Weichselbaumer, G.; Paciello, R. A.; Fischer, R. A.; Herdtweck, E.; Okuda, J.; Marz, D. W. *Organometallics* **1990**, *9*, 489. (k) Anhaus, J. T.; Kee, T. P.; Schofield, M. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642. (l) Schofield, M. H.; Kee, T. P.; Anhaus, J. T.; Schrock, R. R.; Johnson, K. H.; Davis, W. M. *Inorg. Chem.* **1991**, *30*, 3595. (m) Leung, W.-H.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem Soc., Dalton Trans.* **1991**, 2791. (n) Sundermeyer, J. *Chem. Ber.* **1991**, *124*, 1977. (o) Green, M. L. H.; Hogarth, G.; Saunders, G. C. *J. Organomet. Chem.* **1991**, *421*, 233.

Table V. Products that Arise from the Reaction of Cr^+–Zn^+ with $C_2H_5CH(CD_3)NCO$ (**2a**)[a]

	Cr^+	Mn^+	Fe^+	Co^+	Ni^+	Cu^+	Zn^+
$M(HNCO)^+$	86	89	87	82	83	87	84
$M(DNCO)^+$	14	11	13	18	17	13	16
HNCO	85	98	95	90	90	91	96
DNCO	15	2	5	10	10	9	4
HNCO, H_2			48	40	44		
[DNCO, H_2]			52	60	56		

[a] Intensities are normalized to 100% for each neutral loss. Square brackets indicate uncertain labeling distributions among the neutrals.

Table VI. Products that Arise from the Reaction of Ti^+ and V^+ with $C_2H_5CH(CD_3)NCO$ (**2a**)[a]

	Ti^+	V^+
$M(HNCO)^+$	78	83
$M(DNCO)^+$	22	17
HNCO, H_2		10
[DNCO, H_2]		90
CO, CD_3H	100	100
CO, C_2H_6	100	100
CO, H_2		91
CO, HD		9
CO, $2H_2$	100	
CO, CD_3H, H_2	100	
[C_2H_5D]	100	

[a] Intensities are given in $\sum$ products = 100%. Square brackets indicate uncertain labeling distributions among the neutrals.

[MNCO] in the case of Ni^+ and Zn^+ and $MC_4H_6^+$ by loss of $HNCO/H_2$ for Fe^+–Ni^+ (eq 8). Double-resonance experiments[15]

$$M^+ + s\text{-BuNCO} \rightarrow MC_4H_6^+ + HNCO + H_2 \qquad (8)$$

with the $MC_4H_8^+$ ions (M = Fe, Co, Ni) prove that two separate particles are lost and that HNCO loss precedes loss of H_2. The reason for this reaction being absent in the case of **1** is due to the fact that a favorable 1,3-diene complex cannot be formed in that case. Formation of $C_4H_9^+$ by loss of [MNCO] can be rationalized by dissociation of the ion/dipole complex [$C_4H_9^+$- - -NCOM] which becomes more and more exothermic with increasing stability of the carbenium ion. This will even become more evident for the tertiary isocyanates discussed below and is in fact one indication that indeed the ion/dipole and not the insertion/β-hydrogen shift mechanism is operative.

Inspection of the results for $C_2H_5CH(CD_3)NCO$ (**2a**) in Table V reveals no significant differences to the labeled isopropyl isocyanates in Table III. The reader will notice that the ratios of $M(HNCO)^+/M(DNCO)^+$ to HNCO/DNCO are different in most cases. This is not very surprising, and the agreement for Cr^+, for instance, is in fact coincidental as they arise from different processes (Scheme IV). As the H transfer involves the methylene group and leads to the more stable 2-butene complexes, it is favored over D transfer from the methyl group leading to 1-butene complexes.[28-30] Similarly, k_{3H} should be larger than k_{3D} as **18** is more stable than **20**. Furthermore, if isotope effects are taken into consideration, the picture becomes even more complicated and thus no quantitative data can be extracted from Table V. Loss of $HNCO/H_2$ involves scrambling of the hydrogen atoms of the butene moieties as one would otherwise expect exclusively [H_2-DNCO] loss. This finding is in line with studies on butene dehydrogenation which arrived at the same conclusion.[31]

Scheme V. Formation of Nitrile Complexes in the Reactions of Ti^+ and V^+ with *s*-BuNCO (**2**), Presented for the Labeled **2a**

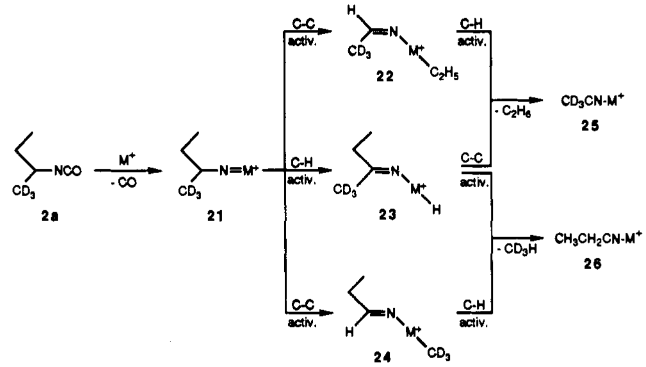
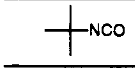


Table VII. Products that Arise from the Reaction of Ti^+–Zn^+ with *tert*-Butyl Isocyanate (**3**)[a]

	Ti^+	V^+	Cr^+	Mn^+	Fe^+	Co^+	Ni^+	Cu^+	Zn^+
$M(HNCO)^+$	65	56	70	73	50	57	50	64	53
HNCO		7	23	17	23	14	33	21	20
HNCO, H_2	3	7							
[MNCO]	9	9	7	10	27	30	17	15	25
[MHNCO]									2
CO, H_2		8							
H_2		3							
$2H_2$		3							
H_2, CH_4	8								
[C_3H_6]	4								
[C_2H_4O]	8								
[C_5H_8O]	3	3							
[C_5H_9N]	*b*	4							

[a] Intensities are given in $\sum$ products = 100%. [b] Present in significant amounts (≈15% of the total ions) but probably due to reaction of Ti^+ with H_2O. See discussion for **1**.

As already mentioned, Ti^+ and V^+ behave very differently from the other first-row ions. Although both of them form $MHNCO^+$ ions, and Ti^+ yields $C_4H_9^+$ while V^+ yields the butadiene complex $VC_4H_6^+$, the majority of the products are due to decarbonylations in combination with other losses. Higher amounts of $TiHNCO^+$ and [TiNCO] can probably be ascribed to the greater oxophilicity of this metal ion as compared to V^+. More insight into the reactions is obtained from the labeling distributions for **2a** given in Table VI.

It can be seen that the formation of nitrile complexes is again highly specific and produces exclusively CD_3CN-M^+ and C_2H_5CN-M^+ as shown in Scheme V. The other processes are, with the exception of the $MHNCO^+$ formation and the $HNCO/H_2$ loss, also specific. The methyl substituent does not seem to be involved in the combined decarbonylation/dehydrogenations, but neither can we envision a mechanism with the limited labeling data nor did the intensity of these products allow characterization with CID. The [CO, CH_4, H_2] loss most likely produces an acrylonitrile complex as double-resonance experiments

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(28) Taking the *absolute* intensities of the four products we are able to determine k_{1H}/k_{1D} for Cr^+, Mn^+, Cu^+, and Zn^+. For Fe^+–Ni^+ the secondary decompositions of the $MC_4H_8^+$ ions according to eq 8 preclude this procedure. We arrive at k_{1H}/k_{1D} = 6.1 (Cr^+), 10.1 (Mn^+), 7.3 (Cu^+), and 8.0 (Zn^+). For the other three ions limiting values of >2.0 (Fe^+), >3.0 (Co^+), and >3.9 (Ni^+) are obtained. Neglecting isotopically sensitive branching ("metabolic switching")[29] due to the isotope effects involved, as well as the statistical factor of 2:3, these values can be interpreted as the preference of the individual metal ions for methylene over methyl hydrogen transfer. For insertion/β-H shift mechanisms this has been demonstrated before,[30] though not always quantitatively.

(29) (a) Harada, N.; Miwa, G. T.; Walsh, J. S.; Lu, A. Y. H. *J. Biol. Chem.* **1984**, *259*, 3005. (b) White, R. E.; Miller, J. P.; Favreau, L. V.; Bhattacharyya, A. *J. Am. Chem. Soc.* **1986**, *108*, 6024. (c) Jones, J. P.; Korzekwa, K. R.; Rettie, A. E.; Trager, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 7074. (d) Guengerich, F. P.; Peterson, L. A. Böcker, R. H. *J. Biol. Chem.* **1988**, *263*, 8176. (e) Prüsse, T.; Fiedler, A.; Schwarz, H. *Helv. Chim. Acta* **1991**, *74*, 1127.

(30) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (b) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (c) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736. (d) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197. (e) Eller, K.; Drewello, T.; Zummack, W.; Allspach, T.; Annen, U.; Regitz, M.; Schwarz, H. *J. Am. Chem. Soc.* **1989**, *111*, 4228.

(31) (a) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624. (b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484.

Table VIII. Products that Arise from the Reaction of Ti^+–Zn^+ with *tert*-Pentyl Isocyanate (**4**)[a]

	Ti^+	V^+	Cr^+	Mn^+	Fe^+	Co^+	Ni^+	Cu^+	Zn^+
$M(HNCO)^+$	62	50	80	78	54	51	51	54	46
HNCO			16	14	4	1	2	17	16
HNCO, H_2	3	17			1	4	3		
HNCO, CH_4					3	7	9		
HNCO, C_2H_4					7	2	2		
[MNCO]	9	13	4	8	31	35	33	29	32
[MHNCO]									6
CO, H_2		8							
CO, $2H_2$	2	2							
H_2		2							
$2H_2$	2	3							
$3H_2$	2	2							
$[C_2H_6]$	4								
$[C_2H_8]$	3								
$[C_2H_6O]$	2								
$[C_4H_8O]$	4	1							
$[C_6H_{10}O]$	3	2							
$[C_6H_{11}N]$	5								

[a] Intensities are given in $\sum$ products = 100%.

with $Ti(C_2H_5CN)^+$ reveal loss of H_2 in the last step. The $[C_2H_6]$ loss furnishes vinyl isocyanate by either ethane elimination or ethene loss followed by dehydrogenation.

***tert*-Butyl Isocyanate.** The results for *t*-BuNCO (**3**) are given in Table VII and can be summarized as follows. Formation of $MHNCO^+$ is the dominant product for *all* metal ions, but while for Cr^+–Zn^+ HNCO loss is important, too, for Ti^+ and V^+ this product is much less intense (V^+) or even absent (Ti^+). Both ions do, however, show loss of $HNCO/H_2$, and this finding is in accord with the generally high amount of multiple losses exhibited by early transition-metal ions.[5] None of the late transition-metal ions form $MC_4H_6^+$ complexes which again is not unexpected, as this would imply either formation of trimethylenemethane complexes or a rearrangement of the carbon skeleton. A drastic increase of the [MNCO] products driven by the formation of the stable t-$C_4H_9^+$ cation is notable. Zn^+ also forms a small amount of $C_4H_8^{\bullet+}$ by formal loss of [MHNCO]; however, this is probably better described as loss of a hydrogen atom from $C_4H_9^+$ ions formed with excess energy.

Ti^+ and V^+ again reveal a pronouncedly different character in that they form a plethora of products besides the ones arising from the ion/dipole mechanism. We will refrain from suggesting any mechanisms which would be highly speculative and hard to substantiate anyway. We stress, however, that no CH_3CN–M^+ complexes by loss of C_2H_6 are formed and will come back to this point in the comparison section.

***tert*-Pentyl Isocyanate.** *tert*-Pentyl isocyanate (**4**) resembles its lower homolog **3** in its behavior as can be seen from the data for Ti^+–Zn^+ in Table VIII. The main product is once again $M(HNCO)^+$ for all metal ions, but while Ti^+ and V^+ do form no less than 12 (Ti^+) and 10 (V^+) product ions, for the late transition-metal ions there are clearly not quite that many.

For Cr^+–Zn^+ all products can be related to the ion/dipole mechanism as evidenced by the results for the labeled compounds **4a–c** in Table IX. The labeling distributions for the individual products are remarkably similar for the different metal ions, and only small differences can be extracted from the data set in the case of the $M(HNCO)^+$ products. As **4c** clearly shows, the terminal methyl group does not participate in the H-transfer step, so only the β-methyl and β-methylene hydrogens need to be considered. For the d_6-labeled compound **4b**, a reversal of the $M(HNCO)^+$ to $M(DNCO)^+$ ratio is noted for Co^+, Ni^+, and Cu^+ which might be interpreted in terms of a preference to form the geminally disubstituted 2-methyl-1-butene in lieu of the trisubstituted 2-methyl-2-butene. If the statistical 1:3 ratio is considered though, all ions still favor β-hydrogen transfer from methylene over methyl groups. The $M(HNCO)^+/M(DNCO)^+$ and HNCO/DNCO ratios are different again, as they are linked to the formation of different products (cf. Scheme IV).[32]

Loss of $HNCO/H_2$ probably proceeds in analogy to eq 8 although we are unable to support this by double-resonance experiments. Obviously, the subsequent dehydrogenation of the initially formed pentene complexes is too rapid to be influenced by ejection pulses. Loss of $HNCO/H_2$ and [DNCO, HD] from **4b** and specific loss of [HNCO, HD] from **4c** demonstrate that only the allylic positions[33] are involved in the scrambling process. For the $HNCO/CH_4$ loss, at least in the case of Ni^+, double resonance established that the resulting $MC_4H_6^+$ ions are formed by demethanation of the HNCO loss product. In view of the very similar labeling distributions, we assume that the same is true also for Fe^+ and Co^+. The resulting product ions are, however, not 1,3-butadiene complexes as evidenced by the exclusive loss of $HNCO/CH_4$ from **4c**. The three most likely candidates are 1,2-butadiene, 1-butyne, and 2-butyne. Absence of $DNCO/CD_4$ loss from **4b** might point against 1-butyne, but in this case one has to assume that scrambling of the allylic hydrogens occurs to explain the $[DNCO/CH_3D]$ loss from **4a**. This is a resonable assumption, though, as we know this exchange process already to be active from the $HNCO/H_2$ loss. Formation of $MC_3H_6^+$ ions by loss of $HNCO/C_2H_4$ is also a consecutive loss; ethene is subsequently eliminated from the $MC_5H_{10}^+$ ions formed by loss of HNCO. In the case of Fe^+ we were able to demonstrate this by double-resonance experiments, and by analogy the same is assumed for the other two ions. Here as well, exchange of the allylic hydrogen atoms seems to precede the ethene loss, and the terminal methyl group is again not involved in the case of Co^+ and Ni^+ as evidenced by the specific loss of $[HNCO/C_2H_2D_2]$ for **4c**; Fe^+ shows a different behavior.

With regard to the $M(HNCO)^+$ products and the losses of $HNCO/H_2$ in the case of Ti^+ and V^+, inspection of Table X reveals differences to the late transition-metal ions. While the $M(HNCO)^+$ ions seem to be formed by the same mechanism, the $HNCO/H_2$ loss shows different patterns for Ti^+ and V^+, each of which are different from those of the other ions. The results can be explained if 2-methyl-1,3-butadiene complexes are formed without scrambling of the allylic hydrogens for Ti^+ and with scrambling of all positions for V^+.

We are unable to provide a mechanism for the generation of the $MC_5H_9N^+$ and $MC_5H_7N^+$ ions by loss of CO/H_2 and $CO/2H_2$, respectively. Extensive scrambling seems to be involved, and the labeling distributions in addition differ between Ti^+ and V^+. It was impossible to derive a mechanism for the formation of the $TiC_4H_5NO^+$ and $TiC_4H_3NO^+$ ions generated by loss of $[C_2H_6]$ and $[C_2H_8]$, but the former process is definitely not a simple 1,2-elimination of ethane. For the $[C_2H_6O]$ loss all that can be said is that one of the two α-methyl groups is lost while the other is retained, and no scrambling is observed for either of them.

The formation of $MC_2H_3N^+$ ions by loss of $[C_4H_8O]$ is again specific for both metal ions. For **4a**, a roughly 1:1 mixture of $MC_2H_3N^+$ and $MC_2D_3N^+$ is formed, while **4b** exclusively forms $MC_2D_3N^+$, and **4c** exclusively forms $MC_2H_3N^+$. The idea of acetonitrile complexes seems obvious, and indeed, if one imagines C_2H_4 loss with concomitant isopropyl isocyanate formation, the observed labeling distribution is precisely the one Scheme III would predict. We therefore describe this loss as $C_2H_4/CO/CH_4$ elimination which accounts for the small magnitude of this product.

Comparison of the Isocyanates 1–4. In comparing the four isocyanates studied, one clearly observes a consistent picture. The late transition-metal ions Cr^+–Zn^+ all react very similarly with the sole exception that Fe^+–Ni^+ sometimes show secondary decompositions not present with the other ions. This uniformity in behavior is another bit of evidence that indeed the ion/dipole mechanism is operative. The usually observed[5] large differences

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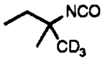
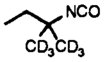
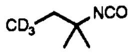
[32] From the absolute intensities (cf. ref 28) in the case of **4b** we determine the preferences of transfer from CH_2 (k_{1H}) over CD_3 (k_{1D}) as k_{1H}/k_{1D} = 1.5 (Cr^+, Mn^+), >0.8 (Fe^+), >0.6 (Co^+), >0.7 (Ni^+), 1.1 (Cu^+), and 1.8 (Zn^+). The statistical factor of 2:6 is again not included.

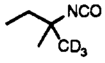
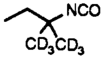
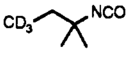
[33] With allylic we refer to the C_1 and C_3 positions in the 2-methylbutenes. Of course C_4 is also allylic in the case of 2-methyl-2-butene, but there are no allylic hydrogens on C_2 to exchange with.

Table IX. Products that Arise from the Reaction of Cr^+–Zn^+ with Labeled *t*-PentNCO Isotopomers **4a–c**[a]

reaction products	 (**4a**)							 (**4b**)							 (**4c**)						
	Cr^+	Mn^+	Fe^+	Co^+	Ni^+	Cu^+	Zn^+	Cr^+	Mn^+	Fe^+	Co^+	Ni^+	Cu^+	Zn^+	Cr^+	Mn^+	Fe^+	Co^+	Ni^+	Cu^+	Zn^+
$M(HNCO)^+$	82	75	85	80	80	76	89	55	57	60	43	49	45	62	100	100	100	100	100	100	100
$M(DNCO)^+$	18	25	15	20	20	24	11	45	43	40	57	51	55	38							
HNCO	80	93	90	80	82	83	92	72	76	75	67	66	71	77	100	100	100	100	100	100	100
DNCO	20	7	10	20	18	17	8	28	24	25	33	34	29	23							
HNCO, H_2			75	65	58					*b*	22	16									
[DNCO, H_2]			25	35	42					*b*	62	64					100	100	100		
[DNCO, HD]										*b*	16	20									
HNCO, CH_4			*c*	6	6												100	100	100		
[DNCO, CH_4]			39	35	30																
[DNCO, CH_3D]			44	40	32																
[HNCO, CD_3H]			17	19	32					60	57	54									
[DNCO, CD_3H]										40	43	46									
HNCO, C_2H_4			12	17	16												9				
[DNCO, C_2H_4]			49	34	27					11	12	*c*					27				
[HNCO, $C_2H_2D_2$]			39	49	57					54	65	71					64	100	100		
[DNCO, $C_2H_2D_2$]										35	24	29									

[a] Intensities are normalized to 100% for each neutral loss. Square brackets indicate uncertain labeling distributions among the neutrals. [b] Signal-to-noise ratio not sufficient for exact determination. [c] Possibly too weak to be detected.

Table X. Products that Arise from the Reaction of Ti^+ and V^+ with the Labeled *t*-PentNCO Isotopomers **4a–c**[a,b]

reaction products	 (**4a**)		 (**4b**)		 (**4c**)	
	Ti^+	V^+	Ti^+	V^+	Ti^+	V^+
$M(HNCO)^+$	80	83	62	54	100	100
$M(DNCO)^+$	20	17	38	46		
HNCO, H_2	66	57		10		21
[DNCO, H_2]	34	39	100	63	100	79
[DNCO, HD]		4		27		
CO, H_2		60		20		18
CO, HD		40		80		82
CO, $2H_2$		36		42		33
CO, H_2, HD	75	64	29	33	100	67
[CO, 2HD]	25		46	25		
CO, HD, D_2			25			
[C_2H_5D]	62				34	
[$C_2H_4D_2$]	38		34		50	
[$C_2H_3D_3$]			50		16	
[$C_2H_2D_4$]			16			
[C_2H_7D]	33					
[$C_2H_6D_2$]	18				<8	
[$C_2H_5D_3$]	49				>92	
[$C_2H_4D_4$]			63			
[$C_2H_3D_5$]			37			
[C_2H_6O]	53					
[C_2H_5DO]					43	
[$C_2H_4D_2O$]					57	
[$C_2H_3D_3O$]	47		100			
[C_4H_8O]	54	~50				
[$C_4H_5D_3O$]	46	~50	100	100	100	100

[a] Intensities are normalized to 100% for each neutral loss. Square brackets indicate uncertain labeling distributions among the neutrals. [b] The intensity of the dehydrogenation products was too low for an exact determination due to severe overlap of the $MC_6H_{9-x}D_xNO^+$, $MC_6H_{7-y}D_yNO^+$, and $MC_6H_{5-z}D_zNO^+$ multiplets.

between Cr^+, Mn^+, Cu^+, and Zn^+ on one side and Fe^+–Ni^+ on the other side are absent in the present system, and this can only be explained with a simple mechanism. Ions like Cr^+ and Cu^+ with a half-filled or filled d-shell, for instance, are unlikely to undergo oxidative addition, as the insertion/β-hydrogen shift mechanism would demand, with the same ease as Fe^+, Co^+, or Ni^+. The ion/dipole mechanism avoids any insertion steps and has been previously shown to apply in other systems for the d^5, d^5s^1 or d^{10}, $d^{10}s^1$ ions.[10,17c–e,20b–d] As rightly pointed out by a referee, alkali-metal ions, or perhaps even protons, could also be expected to react in a similar way (see however Note Added in Proof). $M(HNCO)^+$ ions and HNCO are formed from all isocyanates, and there are evidently no large differences in the labeling distributions of the deuterium-containing compounds. The branching ratios merely reflect the different stabilities of the products formed. With the tertiary isocyanates, there is also a significant amount of carbenium ions formed by loss of [MNCO] which points to a direct separation of the ion/dipole intermediates fueled by the stability of the tertiary cations thus generated. For Fe^+–Ni^+, some of the $M(alkene)^+$ complexes still have enough energy for further decomposition and small neutrals (H_2, CH_4, and C_2H_4) are lost for **2** and **4**. The propene complexes arising from the reaction with **1** and the isobutene complexes from **3** are stable against further degradation.

Ti^+ and V^+ show a distinctly different reactivity than the other ions. A multitude of small products are always generated, and the main decomposition pathway for secondary isocyanates is the formation of nitrile complexes. This novel process involves an initial decarbonylation followed by a 1,1-elimination of an alkane. With tertiary isocyanates the main products are $M(HNCO)^+$ ions just as for the late transition-metal ions, and nitrile products are absent with the exception of the small amount of acetonitrile complexes formed from **4**. In this special case, ethene elimination proceeds, however, and generates a secondary isocyanate, viz. **1**. The absence of nitriles is evidence that one of the bonds to be broken on the α carbon in the course of the 1,1-elimination has to be a C–H bond. In the competition between the C_2H_5 and the CH_3 groups on **2**, elimination of ethane is favored. Unfortunately this still does not enable us to decide whether C–H or C–C activation proceeds right after the initial decarbonylation.

Comparison of the Metal Ions. Why do the early transition-metal ions Ti^+ and V^+ readily form nitrile complexes from secondary isocyanates while the late transition-metal ions Cr^+–Zn^+ are completely unable to do so? It is most certainly not the stability of the final products that is responsible for the difference. Actually, Cr^+–Zn^+ are well-known to form very stable nitrile complexes while V^+ has rarely and Ti^+ has never been observed to form $M(RCN)^+$ complexes with nitriles in primary or secondary reactions.[10,20c,34] As the tertiary isocyanates show, Ti^+ and V^+ may well form $M(HNCO)^+$ ions so that these can be excluded from the discussion as well. *The stability of the intermediate*

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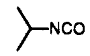
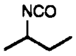
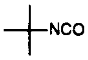
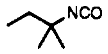
Table XI. Products that Arise from the Secondary Reactions of $M(HNCO)^+$ and $M(C_nH_{2n})^+$ (M = Cr–Zn) with Isocyanates **1–4** According to Equations 15–18, 23, and 24[a]

	 (1)				 (2)					 (3)				 (4)					
	$M(HNCO)^+$		$M(C_3H_6)^+$		$M(HNCO)^+$		$M(C_4H_8)^+$			$M(HNCO)^+$		$M(C_4H_8)^+$		$M(HNCO)^+$			$M(C_5H_{10})^+$		
	eq 15	eq 16	eq 17	eq 18	eq 15	eq 16	eq 17	eq 18	eq 23	eq 15	eq 16	eq 17	eq 18	eq 15	eq 16	eq 24	eq 17	eq 18	eq 23
Cr^+	100		100		100		100			90	10	83	17	82	18		84	13	3
Mn^+	100		100		100		100			100		100		100			100		
Fe^+	89	11	83	17	78	22	71	20	9	53	47	27	73	20	26	54		67	33
Co^+	56	44	91	9	37	63	100			33	67	62	38	26	37	37	*b*	*b*	*b*
Ni^+	50	50	100		40	60	91	9		43	57	60	40	29	47	24	*b*	*b*	*b*
Cu^+	53	47	100		25	75	96	4		26	74	83	17	24	76			100	
Zn^+	100		100		100		100			100		100		100			100		

[a] Intensities are given in $\sum$ products = 100%. [b] The intensity of the $MC_5H_{10}^+$ ions was too low to allow for secondary reactions being studied.

nitrene complexes therefore could be the pivotal point we are left with.

Indeed, the binding energies (BE's) of both metal ions to the simplest nitrene, NH, have been determined to be quite strong, namely $D°(HN{=}Ti^+) = (466 \pm 12)$ kJ mol^{-1}[35] and $D°(HN{=}V^+) = (415 \pm 15)$ kJ mol^{-1}.[36] This is opposed to Fe^+, which has been found to possess a much weaker binding energy ($D°(HN{=}Fe^+) = (230 \pm 60)$ kJ mol^{-1}).[37] Cr^+–Cu^+ are also unreactive with ammonia[11,37,38] while Sc^+–V^+ are able to exothermically dehydrogenate NH_3 to form $HN{=}M^+$ nitrene complexes.[35–37,39] In the absence of any barriers, this might be tentatively interpreted as $D°(HN{=}M^+) < 390$ kJ mol^{-1} for M = Cr–Cu.

Relation to Condensed-Phase Systems. The finding that metal ions with high BE's for nitrenes can react to form nitrile complexes and those with substantially weaker BE's are unable to do so sheds some new light on the surface-catalyzed process where nitrene intermediates[40] are formed on the Ni_x/C_∞ system as well (Scheme I).[7] Another parallel is that the heterogeneous catalyst is also unable to induce decarbonylation/alkane loss from tertiary isocyanates but catalyzes the formation of alkenes and HNCO instead. The latter process closely resembles eqs 3 and 4 and the analogous reactions of the other isocyanates. We therefore feel confident to assume similar mechanisms to be operative. If we hence presume that the crucial factor of the binding energies can be directly transcribed into the condensed-phase studies, we may conclude that catalysts with high BE's for surface nitrenes should work best for the formation of nitrile complexes. We also predict that **2** would give propio- and acetonitrile with Ni_x/C_∞. Using $(C_2H_5)_2CHNCO$ might be a way to product propionitrile selectively.

The reactions of HNCO with several supported and unsupported metal surfaces have been studied, but in this case initial cleavage to [Surf]–H and [Surf]–NCO is observed.[41] Isocyanate surface species are also formed in the reaction of NO and CO with a large variety of metal catalysts, and in some cases reversible dissociation to [Surf]–N and [Surf]–CO has been postulated.[41i,42] They are also formed from NH_3 or N_2H_4 and CO[19,41j,k,43] and may provide a clue as to how alkenes and HNCO are produced. Cleavage of the isocyanates into [Surf]–R and [Surf]–NCO could be followed by decomposition of the surface-bound alkyl groups into alkenes and [Surf]–H. Final combination of [Surf]–H and [Surf]–NCO to HNCO has been shown to be operative.[41a,d,e,g,j] The similarity to the ion/dipole mechanism is obvious.

Further information relevant for the discussion about the nitrile formation is obtained from adsorption studies of CH_3NCO on single-crystal surfaces. While adsorbed methyl isocyanate desorbs non-dissociatively upon heating of a Cu(100) surface, for potassium-dosed Cu(100) or clean Pt(110) dissociation into adsorbed CH_3N and CO is observed.[44] This difference has been explained by the adsorption energies, which make the CH_3N–CO cleavage exothermic in the case of Pt(110) and endothermic in the case of Cu(100). The added potassium increases the CO bonding so that the reaction is possible here as well. These results completely support our conclusion that it is the nitrene binding energy that is important for the nitrile formation. Our proposal, that catalysts with high BE's for surface nitrenes should work best, could thus

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be tested with Pt(110) or Cu(100)/K. Another possibility would be, for instance, Fe(111) or Fe(100) for which it has been estimated that the strength of the Fe–NH_{ad} bond is in the order of about 420 kJ mol^{-1} [45] and hence is similar to bare Ti^+ or V^+.

Secondary Reactions. While in the course of every ICR study a multitude of secondary reactions has to be studied to unambiguously identify the primary products as such, and higher-order processes may be followed according to the will (and perseverance) of the operator, usually their outcome is not as exciting as that of the primary reactions. We will therefore spare the reader (and ourselves!) from discussing all of the hundreds of follow-up reactions that have been noted during this study. And yet, some of them bear some interesting findings. In the case of V^+, for instance, it can be seen that nitrile formation is not limited to the highly reactive, "bare" metal ions but that the nitrile complexes themselves can react accordingly (eqs 9–14). Another observation

$$V(CH_3CN)_n^+\ (n = 0\text{–}2) + i\text{-PrNCO} \rightarrow V(CH_3CN)_{n+1}^+ + CO + CH_4 \quad (9)$$

$$V(CH_3CN)^+ + s\text{-BuNCO}$$

$$\rightarrow VO(CH_3CN)^+ + [C_5H_9N] \quad (7\%) \quad (10)$$

$$\rightarrow V(CH_3CN)_2^+ + CO + C_2H_6 \quad (65\%) \quad (11)$$

$$\rightarrow V(CH_3CN)(C_2H_5CN)^+ + CO + CH_4 \quad (28\%) \quad (12)$$

$$V(C_2H_5CN)^+ + s\text{-BuNCO}$$

$$\rightarrow V(CH_3CN)(C_2H_5CN)^+ + CO + C_2H_6 \quad (21\%) \quad (13)$$

$$\rightarrow V(C_2H_5CN)_2^+ + CO + CH_4 \quad (79\%) \quad (14)$$

from these reactions is the higher specificity with which they proceed. While in the primary reactions 7 (**1**) or 5 (**2**) products are observed for V^+, the ligated ions almost specifically produce bis(nitrile) complexes. The only exception is a small amount of oxidized ions in the case of **2**. This is a general finding[46] and is probably due to the fact that the available energy in the collision complex is partly dissipated by the attached ligand. With the labeled isocyanates the expected shifts are found. No label incorporation is seen with **1a**, in the analog of eq 9, while **1b** forms a triplet of peaks for the bis(nitrile) and a quartet for the tris(nitrile) complex, corresponding to 0, 3, 6, and 9 deuterium atoms. All six deuterium atoms of the two molecules **2a** end up in the vanadium bis(acetonitrile) ion, three in the mixed, and none in the bis(propionitrile) complex (see eqs 11–14).

For Cr^+–Zn^+ the secondary reactions reveal interesting aspects with regard to the formation of adduct complexes via ligand-exchange reactions. As these adducts are used as precursors in the sector-instrument approach to gas-phase organometallic chemistry for metastable ion (MI)[47] and high-energy CID[48] spectra, we will briefly present our observations.

With isopropyl isocyanate the initially formed $M(HNCO)^+$ and $M(C_3H_6)^+$ ions (M = Cr–Zn) react according to eqs 15–18 (Table XI). As can be seen from Table XI, $MC_4H_7NO^+$ ions are the main, if not exclusive, products formed in the secondary reactions of **1**. There are two reasonable structures for these ions, either $M(i\text{-}C_3H_7NCO)^+$ adducts or "dissociated" $M(HNCO)(C_3H_6)^+$ complexes. The two possibilities can be distinguished with the help of the deuterium-labeled compounds. In the case of **1a**, the primarily formed $M(HNCO)^+$ and $M(C_3H_5D)^+$ ions (eqs 5 and 6) exclusively afford $MC_4H_6DNO^+$ in their secondary reactions which is in accord with either structure. The distinction is achieved with **1b** whose primary reactions resulted in the formation of $M(HNCO)^+$, $M(DNCO)^+$, $M(C_3H_3D_3)^+$, and $M(C_3H_4D_2)^+$ ions. The secondary reactions of these ions are metal-ion dependent and two groups are observed. The first group is formed by Cr^+, Mn^+, and Zn^+, for which the reactions in eqs 16 and 18 are not observed and where hence $MC_4H_7NO^+$ is the sole secondary product for **1**. Upon reaction with **1b**, a shift to $MC_4H_4D_3NO^+$ demonstrates that eqs 15 and 17 can be regarded as simple ligand-exchange reactions (eqs 19 and 20).

$$M(HNCO)^+ + C_nH_{2n+1}NCO$$

$$\rightarrow MC_{n+1}H_{2n+1}NO^+ + HNCO \quad (15)$$

$$\rightarrow M(HNCO)_2^+ + C_nH_{2n} \quad (16)$$

$$M(C_nH_{2n})^+ + C_nH_{2n+1}NCO$$

$$\rightarrow MC_{n+1}H_{2n+1}NO^+ + C_nH_{2n} \quad (17)$$

$$\rightarrow M(C_nH_{2n})_2^+ + HNCO \quad (18)$$

$$M(HNCO)^+ + i\text{-PrNCO} \rightarrow M(i\text{-PrNCO})^+ + HNCO \quad (19)$$

$$M(C_3H_6)^+ + i\text{-PrNCO} \rightarrow M(i\text{-PrNCO})^+ + C_3H_6 \quad (20)$$

For Fe^+–Cu^+ there is already a difference in the secondary reactions of the unlabeled **1** in that the reaction in eq 16 is always observed and eq 18 is seen at least for Fe^+ and Co^+. Lack of observation of the latter for Ni^+ and Cu^+ can probably be attributed to the small abundance of the $M(C_3H_6)_2^+$ as a consequence of the already small yield of $M(C_3H_6)^+$ precursor ions. Upon reaction with **1b** three isotopomers are found in eqs 15 and 17, i.e., $MC_4H_{7-x}D_xNO^+$ (x = 2–4). This can only be rationalized if it is assumed that, at least in part, "dissociated" complexes are formed (eqs 21 and 22). Hence, $MC_4H_5D_2NO^+$ is in fact

$$M(HNCO)^+ + i\text{-PrNCO} \rightarrow M(HNCO)(C_3H_6)^+ + HNCO \quad (21)$$

$$M(C_3H_6)^+ + i\text{-PrNCO} \rightarrow M(HNCO)(C_3H_6)^+ + C_3H_6 \quad (22)$$

$M(HNCO)(C_3H_4D_2)^+$, $MC_4H_4D_3NO^+$ is the mixture of $M(DNCO)(C_3H_4D_2)^+$ and $M(HNCO)(C_3H_3D_3)^+$, and finally $MC_4H_3D_4NO^+$ is $M(DNCO)(C_3H_3D_3)^+$.

The two classes of metal ions differ also in the CID characteristics of the $MC_4H_7NO^+$ complexes. Two representative examples have been studied: Cr^+ and Fe^+. The $Cr(i\text{-PrNCO})^+$ adduct complex upon CID gives rise predominantly to Cr^+ by ligand detachment, while from $Fe(HNCO)(C_3H_6)^+$ at low energies Fe^+, $Fe(HNCO)^+$, and $Fe(C_3H_6)^+$ are formed in a ratio of about 1:2:2. As expected, the Fe^+ signals gain importance with increasing CID energy.

For *s*-BuNCO very similar results are obtained. In addition to eqs 15–18 a new product is observed, i.e., $Fe(C_4H_6)(C_4H_8)^+$ by loss of H_2 from the bis(alkene) product (eq 23 and Table XI).

$$M(C_nH_{2n})^+ + C_nH_{2n+1}NCO \rightarrow M(C_nH_{2n})(C_nH_{2n-2})^+ + HNCO + H_2 \quad (23)$$

In the M^+/*t*-BuNCO systems only eqs 17 and 18 apply, but for *t*-PentNCO together with eq 23 a further reaction can be noted for the $M(HNCO)^+$ ions (eq 24).

$$M(HNCO)^+ + t\text{-PentNCO} \rightarrow M(C_5H_{10})^+ + 2HNCO \quad (24)$$

With the labeled isocyanates **2a**, **4a**, and **4b**, we observe similar differences in the labeling distribution of the "adduct complexes" as for **1b**. In the case of **2a**, Cr^+, Mn^+, and Zn^+ afford $MC_5H_6D_3NO^+$ as the sole isotopomer in the secondary reactions, thus an intact adduct complex $M(C_2H_5CH(CD_3)NCO)^+$ is formed for these ions. On the contrary, Fe^+–Cu^+ in addition yield $MC_5H_7D_2NO^+$ and $MC_5H_5D_4NO^+$ ions, proving that $M(HNCO)(C_4H_8)^+$ ions are generated. A slightly different pattern is noted for the *tert*-pentyl isocyanates **4a** and **4b**. While Mn^+ and Zn^+ still react by simple ligand exchange, forming only the d_3-(**4a**) or d_6-labeled (**4b**) adduct, respectively, Cr^+ now reveals the same labeling distribution of d_2, d_3, d_4 (**4a**) and d_5, d_6, d_7 (**4b**) isotopomers for the "adduct complex" as do Fe^+–Cu^+.[49] Therefore

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Cr^+ (and Fe^+–Cu^+) ions afford $M(HNCO)(alkene)^+$ complexes in the secondary reactions if a tertiary isocyanate is involved. This conclusion is also supported by the data in Table XI which show that, in contrast to the secondary isocyanates, eqs 16, 18, and 23 are observed for Cr^+ in the case of the tertiary substrates **3** and **4**.

The preceding observations should caution researchers employing sector-field instruments where an ion with an elemental composition corresponding to the adduct complex is selected as precursor for MI or CID studies. These ions are usually formed in chemical ionization (CI) sources by electron impact on a mixture of the substrate and a volatile organometallic complex such as $Fe(CO)_5$. The adduct complex is believed to be formed by simple ligand exchange from $Fe(CO)^+$, for instance. As the present study shows, what appears to be a simple ligand-exchange reaction is not necessarily one. Although, admittedly, the FTICR conditions differ from the high-pressure CI plasma, the occurrence of similar processes would ultimately lead to false conclusions if a dissociated complex was selected from the ion source and erroneously taken to be an intact adduct complex.

Note Added in Proof. The reaction of Na^+ and K^+ with **2** has now been studied but was found to afford only adduct complexes with a very slow rate. MI spectra of *s*-$BuNCOH^+$, formed with H_2 or *i*-C_9H_{10} CI plasma, result in the exclusive loss of [HNCO]. The latter experiment was done in a four-sector BEBE instrument and the result is completely in line with the known proton affinity of (*E*)-2-butene (PA = 750 kJ mol^{-1})[50] and the estimated value for NCOH (PA ≈ 722 kJ mol^{-1}).[51] The MI spectrum of protonated **2a** accordingly results in loss of [HNCO] only (100%) with any [DNCO] loss being significantly less than 3%, the limit of detectability in this particular experiment.

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Registry No. 1, 1795-48-8; 2, 15585-98-5; 3, 1609-86-5; 4, 1612-71-1; Cr^+, 14067-03-9; Mn^+, 14127-69-6; Fe^+, 14067-02-8; Co^+, 16610-75-6; Ni^+, 14903-34-5; Cu^+, 17493-86-6; Zn^+, 15176-26-8; D_2, 7782-39-0.

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(49) In the case of Fe^+ reacting with **4a**, we were unable to detect the d_2- and d_4-labeled "adduct complexes" owing to their low intensity and the occurrence of isobaric $FeC_8H_{16-x}D_x^+$ ions formed in the reactions of $FeC_3H_{6-y}D_y^+$ with **4a**. The observation of d_5-, d_6-, and d_7-labeled "adducts" in the case of **4b**, however, unambiguously proves that for *t*-PentNCO too, $Fe(HNCO)(alkene)^+$ complexes are formed for Fe^+. For all other metal ions the labeling distributions with **4a** and **4b** were established and found to be according to the expectations.

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Characterization of Hydrogen Bonding in Zeolites by Proton Solid-State NMR Spectroscopy

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Abstract: Variable-temperature magic-angle spinning proton NMR spectroscopy has characterized the structure and dynamics of hydrogen-bonded adsorption complexes between various adsorbates and the Bronsted acid site in a representative zeolite, H-ZSM5. The active site Bronsted proton chemical shift was found to be extremely sensitive to the amount and type of adsorbate introduced. The adsorbates studied were acetylene, ethylene, carbon monoxide, benzene, ethane, and nitrogen, with emphasis on the first four. Slow-exchange spectra obtained at 123 K for loadings of less than 1 equiv showed resolved peaks for free and complexed Bronsted sites. Low-temperature reverse cross-polarization experiments confirm that the adsorbates hydrogen-bond specifically to the Bronsted site and do not interact with the external silanol groups. Fast-exchange-averaged chemical shifts were observed at 298 K. Quantitative treatment of the loading-dependent chemical shifts for acetylene, ethylene, and carbon monoxide yielded equilibrium constants at 298 K of ca. 7, 7, and 0.7 $equiv^{-1}$, respectively. The differences in the observed change in chemical shift with type of adsorbate are explained in terms of hydrogen-bond shifts and established theories of shielding contributions from neighboring group anisotropy effects. A semiquantitative treatment of induced shifts for acetylene, ethylene, and benzene adsorption yielded a characteristic hydrogen-bond distance ranging from 2.35 to 2.78 Å, which is in agreement with gas-phase model compounds and only slightly larger than distances calculated for model clusters using quantum chemical methods. These results suggest that quantitative interpretation of proton chemical shifts for zeolite catalysts provides information on the strength of hydrogen bonds and suggests geometries of the hydrogen-bonded complexes similar to those observed in the gas phase and calculated for model clusters. Furthermore, benzene undergoes rapid deuterium–hydrogen exchange near 298 K, apparently through a hydrogen-bonded intermediate.

Introduction

There is considerable interest in the properties of Bronsted acid sites in zeolite catalysts and their interactions with various adsorbed molecules.[1] The locus of catalytic activity in zeolites is an acidic hydrogen attached to a bridging framework oxygen site within the zeolite channels. Several approaches have been used in attempting to more clearly understand the chemistry that occurs within the zeolite channels at the active site. The most common methods involve either calorimetric or spectroscopic techniques.[1] Enthalpies of adsorption and desorption for bases such as amines are used to measure the apparent strength of interaction and thus provide a measure of some function of catalyst acidity.[2] However,

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