Specific Processes and Scrambling in the Dehydrogenation of Ethane and the Degenerate Hydrogen Exchange in the Gas-Phase Ion Chemistry of the $Ni(C,H_3,O)^+/C_2H_6$ Couple

Short Communication

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Dedicated to Professor *Herbert Mayr* on the occasion of his 60th birthday

A mechanistically unprecedented situation characterizes the gas-phase ion chemistry of $Ni(C,H_3,O)^+$ when reacted under thermal, single-collision conditions with ethane. A dehydrogenation channel leading to $Ni(C_3,H_7,O)^+$ is to 90% preceded by a complete loss of positional identity of all nine H-atoms of the encounter complex ('scrambling'), whereas *ca.* 10% of the reaction exhibit a selective C–H bond activation of the alkane. In addition, a degenerate H exchange between ethane and the (C,H_3,O) unit occurs as a side reaction, the mechanistic details of which remain unknown for the time being.

Introduction. – Pronounced ligand effects have been reported recently in the metal-mediated activation of methane [1]. Whereas ground-state 3d mono-atomic cations, for example, do not bring about thermal C–H bond cleavage [2], NiH^+ activates methane at temperatures as low as 80 K, CoH^+ reacts at room temperature, and for FeH^+ temperatures above 600 K are required for the H/CH_3 ligand exchange (*Eqn. 1*), which is exothermic for all three metal-hydride cations [1a][3]; the reaction has also been observed for the group-10 metal hydrides PdH^+ [1b] and PtH^+ [4]. In addition, depending on the electronic structure of MH^+, the H/CH_3 ligand switch occurs directly or is preceded by partial H-exchange processes [1].

$$MH^+ + CH_4 \longrightarrow M(CH_3)^+ + H_2 \qquad (1)$$

$$M = Fe, Co, Ni, Pd, Pt$$

Exothermicity, however, is not a sufficient criterion to permit for the occurrence of this reaction, because, for several systems with $M^+–L$ bonds weaker than the $M^+–CH_3$ bond, thermal activation of CH_4 does not take place, and the Ni^{II} complexes described in *Eqn. 2* may serve as useful examples. While for the NiL^+ cations with $L = OH$ and OCH_3 the L/CH_3 ligand exchanges are exothermic [5], their non-occurrence points to the existence of kinetic barriers (see also [6]).

$$NiL^+ + CH_4 \not\rightarrow Ni(CH_3)^+ + HL \tag{2}$$

$$L = OH,\ OCH_3$$

Higher alkanes are generally much more reactive than methane – which is most inert of all hydrocarbons – for both the bare and the ligated 3d and 4d transition-metal cations [2]. Whereas being unreactive towards methane, NiL^+ ions ($L = OH, OCH_3$), for example, give rise to a rich gas-phase ion chemistry involving various types of C–H and C–C bond activation when reacted with the alkanes C_nH_{2n+2} ($n = 2-4$) [7].

In this Short Communication, we describe a mechanistically highly unusual case in which various modes of H-transfer processes occur, *i.e.*, scrambling and specific C–H bond activation, in the dehydrogenation of ethane and in a degenerate H-exchange process. The system of interest is the $Ni(C,H_3,O)^+/C_2H_6$ couple, generated and studied under the conditions of electrospray ionization (ESI) mass spectrometry.

Experimental. – The present experiments were performed with a *VG BIO-Q* mass spectrometer of QHQ configuration (Q: quadrupole, H: hexapole) equipped with an ESI source as described in details previously [8][9]. In brief, the complexes having the elemental compositions $Ni(C,H_3,O)^+$ or $Ni(C,D_3,O)^+$ were formed from millimolar solutions of NiX_2 (X = halogen) in CH_3OH or CD_3OD, resp., under relatively harsh ionization conditions (typical cone voltages are around 40–60 V) [10]. After mass selection by means of Q1, the thermalized ions were exposed to react with ethane in the hexapole at r.t. and at pressures in the order of 10^{-4} mbar; this is considered to correspond to nearly single-collision conditions. Ionic products were detected using Q2. The ion-reactivity studies were performed at an interaction energy in the hexapole (E_{lab}) nominally set to 0 eV [4][11]. Collision-induced dissociation (CID) experiments of $Ni(C,H_3,O)^+$ and some isotopologues were performed with Xe as a collision gas at collision energies of $E_{lab} = 10$ eV.

In the computational studies, which only aim at a qualitative understanding of those $Ni(C,H_3,O)^+$ species being relevant in the present context, the geometries were optimized at the B3LYP level of theory [12] as implemented in the Gaussian03 programme package [13], using basis sets of approximately triple-ζ quality. For H- and C-atoms, these were the triple-ζ plus polarization basis sets (TZVP) of *Ahlrichs* and co-workers [14]. The accuracy of this qualitative approach is in the order of ± 20 kJ mol^{-1} for relative energies of isomers [15] (see also [16]), and the nature of the stationary points as minima or saddle points was characterized by frequency analysis.

Results and Discussion. – The thermal ion–molecule reaction of mass-selected $Ni(C,H_3,O)^+$ with C_2H_6 is dominated by single dehydrogenation (*Eqn. 3*); double dehydrogenation amounts to $< 1\%$, as compared to *Eqn. 3*, and is not considered any further here.

$$Ni(C,H_3,O)^+ + C_2H_6 \rightarrow Ni(C_3,H_7,O)^+ + H_2 \tag{3}$$

Isotopic labeling experiments (*Eqns. 4–7*) are quite revealing in that, based on detailed kinetic modeling (for technical details, see [17]), four conclusions emerge and the observed branching ratios for the generation of H_2, HD, and D_2 can best be explained by assuming two parallel reactions: *i*) In a channel of *ca.* 90% weight, all nine H (D) atoms lose their positional identity prior to dehydrogenation ('scrambling'). *ii*) In a 'specific' process, which accounts for *ca.* 10% of the total dehydrogenation, one H (D) atom of ethane and eight statistically equivalent H-atoms combine to molecular hydrogen. *iii*) The kinetic isotope effect (KIE) for the unspecific processes amounts to KIE = 1.6 – 1.7 per D-atom, and for the specific bond activation a value of KIE = 2.3 – 2.9 has been obtained; for the latter, due to its relatively small contribution (*ca.* 10%), the modeling is rather insensitive to variations of the KIE1)*.* *iv*) The observed KIE suggest that breaking of C–H and making of H–H bonds somewhat contribute to the rate-limiting step. These results are consistent with previous KIE data for iron-alkoxide cation systems [18].

	H_2	HD	D_2	
$Ni(C,H_3,O)^+ + C_2D_6 \longrightarrow$	13	59	28	(4)
$Ni(C,D_3,O)^+ + CH_3CD_3 \longrightarrow$	19	56	25	(5)
$Ni(C,D_3,O)^+ + C_2H_6 \longrightarrow$	58	37	5	(6)
$Ni(C,H_3,O)^+ + CH_3CD_3 \longrightarrow$	52	43	5	(7)

As our current experimental set-up does not permit an unambiguous structural characterization of the species involved in the $Ni(C,H_3,O)^+/C_2H_6$ couple, we have addressed part of this complex issue by an exploratory investigation of the $Ni(C,H_3,O)^+$-manifold2) by means of DFT calculations (*Fig.*). The global minimum **1a** corresponds to a complex of triplet NiH^+ ($^3\Delta$) with CH_2O (*Fig.*, *a*). At the theoretical level used, the binding energy of CH_2O amounts to 181 kJ mol^{-1}, and isomerization **1a** → **2a** *via* β-H migration requires 117 kJ mol^{-1} to yield the $Ni(OCH_3)^+$ isomer **2a**, which is less stable than **1a** by 22 kJ mol^{-1}. Two other minima have been located on the triplet surface. One corresponds to the Ni^{II} isomer $Ni(CH_2OH)^+$ (**3**) with a Ni–C bond, and the second to the less stable Ni^I complex **4**, in which Ni^+ interacts with the O-atom of the CH_2OH radical. This structural assignment is supported by the computed spin and charge densities. The spin is nearly equally distributed between the C- and the Ni-atoms of **4**, while most of the charge (82%) is located on the Ni-atom. Isomer **4** is connected with **3** by a transition structure for a haptotropic Ni shift, and, for the isomerization **4** $\rightleftharpoons$ **1a**, we have succeeded in locating an unusual reaction path. This involves a series of ion – dipole complexes [20], *i.e.*, **4** converts to a transition structure in which the Ni-atom interacts weakly with the CH_2OH fragment; the charge is nearly equally distributed between the two building blocks. Next, a H-atom is pulled away to generate a NiH^+/OCH_2 complex which, upon rotation, collapses to **1a**. Note, that the whole transformation **4** → **1a** occurs below the asymptote for generating separated NiH^+ and CH_2O. We have also located a transition structure for the direct conversion **4** → **2a**. However, in line with experimental findings (see below), this high-energy path (38 kJ mol^{-1} above separated NiH^+/OCH_2) is not relevant in the present context.

As to the relevance of the computational findings, we can provide circumstantial experimental evidence for some of the predictions. For example, CID studies of mass-selected $Ni(C,H_3,O)^+$, *m*/*z* 89, give rise to losses of CH_2O (→ *m*/*z* 59), C,H_3,O (→ *m*/*z*

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1) Furthermore, degenerate H-atom exchange as a competitive reaction channel (see below) contributes to 10% error of the relative branching ratios.

2) For a detailed discussion of the structurally related system $Fe(OCH_3)^+ \rightleftharpoons Fe(H)(CH_2O)^+$, see [19].

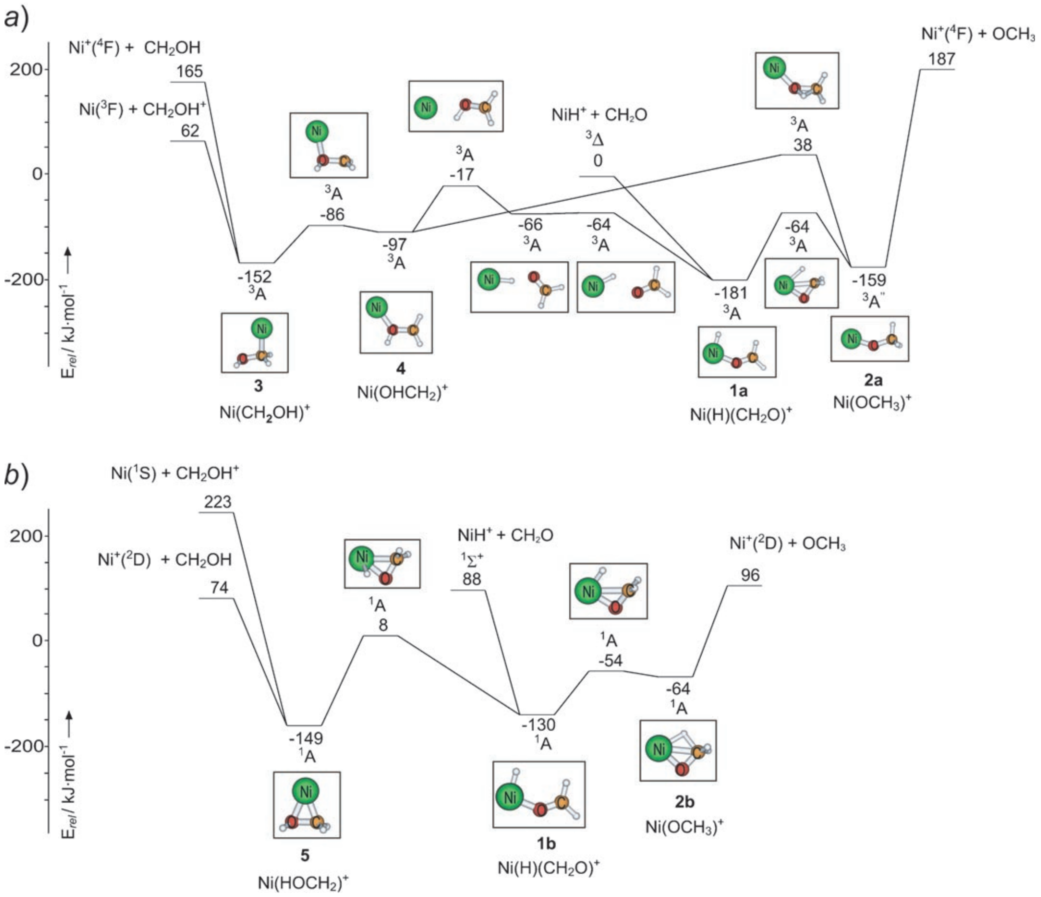

Figure. *DFT-Based energy diagram for various* $Ni(C,H_3,O)^+$ *isomers, their connecting transitions structures, and the asymptotes for ligand losses.* The values are relative to the energies of the separated building blocks $NiH^+(^3\Delta)$ and CH_2O, corrected for contributions of zero-point vibrational energies, and are given in kJ mol^{-1}. *a*) Triplet related species; *b*) singlet electromers.

58), and neutral Ni (→*m/z* 31) in a ratio 1:3:1.4. Based on thermochemical considerations, these three channels are indicative of Ni^+ complexes having the connectivities of $Ni(H)(CH_2O)^+$ (**1a**) and any of the three $Ni(CH_2OH)^+$ isomers **3**, **4**, or **5**. Further, a parent-ion scan[3]) of $Ni(C,H_3,O)^+$, *m/z* 89, identifies four precursors. Whereas three of them, *i.e.*, losses of $\Delta m = 28$ (CO or N_2), $\Delta m = 30$ (CH_2O), and $\Delta m = 32$ (CH_3OH), are not indicative of the structure(s) of the resulting *m/z* 89 ion, elimination of HBr, $\Delta m = 80$ and 82, points to $Ni(Br)(CH_3OH)^+$ as a crucial, structure-

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[3]) In a parent-ion scan, a first analyzer scans a regular mass spectrum, then the reaction of interest is allowed to occur in an intermediate collision cell, while a second mass analyzer is fixed to the mass of the desired product ion. In this way, all ions ('parents') can be identified, which give rise to a particular product ion.

indicative precursor candidate. For example, ESI experiments in which CD_3OH/H_2O or CH_3OD/D_2O were employed as solvents establish a specific activation of the methyl C−H(D) bond of methanol, followed by reductive elimination of HBr (DBr), *i.e.*, the former solvent gives rise to $Ni(C,H,D_2,O)^+$ and the latter to $Ni(C,H_2,D,O)^+$. These findings strongly suggest that initially any of the isomers **3**, **4**, or **5** – perhaps with a preference for **3** – are formed. A fraction of this ion mixture subsequently undergoes isomerization to the **1a**/**2a** manifold. The latter is supported by a CID experiment of the ion $Ni(CD_2OH)^+$, generated *via* DBr elimination from $Ni(Br)(CD_3OH)^+$. Upon CID, in addition to the structure-unspecific losses of $[C,H,D_2,O]$ and neutral Ni, the products NiH^+ (loss of CD_2O) and NiD^+ (elimination of CHDO), formed in a ratio 3 : 1, indicate an isomerization $Ni(CD_2OH)^+ \rightarrow Ni(H)(CD_2O)^+$ (**1a**) rather than a direct conversion $Ni(CD_2OH)^+$ (**4**) $\rightarrow Ni(OCHD_2)^+$ (**2a**). Further, in line with the *Figure*, the complex $Ni(H)(CD_2O)^+$ (**1a**) has two options, *i.e.*, to lose directly CD_2O or, prior to formaldehyde evaporation, to undergo partial, degenerate isomerization according to $Ni(H)(CD_2O)^+ \rightleftharpoons Ni(OCHD_2)^+ \rightleftharpoons Ni(D)(CHDO)^+$.

With regard to the interconversions of $Ni(C,H_3,O)^+$ in addition to the ground-state triplet surface, we have also briefly analyzed the singlet surface of this system (*Fig.*, *b*) in order to probe whether or not the rearrangements are subject to a 'two-state reactivity (TSR)' scenario [21]; the latter has been identified to play a crucial role in the reversible *β*-H transfer between $Fe(C_2H_5)^+$ and $Fe(H)(C_2H_4)^+$ in that a spin flip from the quintet ground-state to the excited triplet surface opens up a pathway with a transition structure which is by 33.5 kJ mol^{-1} lower in energy than the corresponding quintet transition structure [22]. However, as illustrated in the *Figure*, inclusion of the excited singlet surface does not offer an energetic advantage for the $Ni(H)(CH_2O)^+ \rightleftharpoons Ni(OCH_3)^+$ isomerization. In contrast, at the theoretical level used all relevant stationary points are higher in energy for the singlet states as compared to their triplet electromers. A one-state scenario has also been reported for the related $Fe(OCH_3)^+ \rightleftharpoons Fe(H)(CH_2O)^+$ rearrangement [19].

As to the role of singlet states for the isomers **3**, **4**, and **5**, no minima have been located for the ^{1}A-Ni^+ complexes structurally analogous to **3** and **4**. The η^2-bridged structure **5**, however, resides in its ^{1}A state in a rather deep potential well, and it takes 157 kJ mol^{-1} to bring about isomerization of **5** to **1b** (^{1}A).

As to the experimentally observed H scrambling (*Eqns. 4–7*), due to the height of the barrier for the interconversion of the $Ni(C,H_3,O)^+$ isomers, this process is only possible for vibrationally excited ions when formed from the initially generated manifold of the isomers. We note, however, that the energy demand for *β*-H migration in various $M(OCH_3)L$ systems has been reported to highly depend on the presence and nature of additional ligands L [18][19][23]. Thus, the observed scrambling in the $Ni(C,H_3,O)^+/C_2H_6$ couple may well profit energetically from the particular structural and electronic features of for the time being unknown intermediates, and future work is indicated to address this aspect.

In the course of studying the dehydrogenation of C_2H_6, we also observed an exchange of the H-atoms of the $Ni(C,H_3,O)^+$ complex with those of ethane. While this degenerate isomerization remains unnoticed in the unlabeled couple, a few details of the 'hidden' H-atom transfer (for the concept of 'hidden' H-rearrangements, see [24]) can be derived from studying isotopically labeled variants (*Eqns. 8–11*).

$$\mathrm{Ni(C,H_3,O)^+ + C_2D_6} \;-\!\!\left[\begin{array}{ll} \rightarrow \mathrm{Ni(C,H_2,D,O)^+} & 65\% \\ \rightarrow \mathrm{Ni(C,H,D^2,O)^+} & 35\% \end{array}\right. \tag{8}$$

$$\mathrm{Ni(C,D_3,O)^+ + CH_3CD_3} \;-\!\!\left[\begin{array}{ll} \rightarrow \mathrm{Ni(C,H_2,D,O)^+} & 11\% \\ \rightarrow \mathrm{Ni(C,H,D_2,O)^+} & 89\% \end{array}\right. \tag{9}$$

$$\mathrm{Ni(C,D_3,O)^+ + C_2H_6} \;-\!\!\left[\begin{array}{ll} \rightarrow \mathrm{Ni(C,H_2,D,O)^+} & 28\% \\ \rightarrow \mathrm{Ni(C,H,D_2,O)^+} & 72\% \end{array}\right. \tag{10}$$

$$\mathrm{Ni(C,H_3,O)^+ + CH_3CD_3} \;-\!\!\left[\begin{array}{ll} \rightarrow \mathrm{Ni(C,H_2,D,O)^+} & 91\% \\ \rightarrow \mathrm{Ni(C,H,D_2,O)^+} & 9\% \end{array}\right. \tag{11}$$

Some general features of the degenerate H-atom exchange – the exact branching ratios of which vary between 13 and 19% relative to the competitive dehydrogenation channels of ethane (*Eqns. 4–7*) – can be deduced from thermochemical aspects as well as a kinetic modeling of the isotope pattern reported in *Eqns. 8–11*⁴):

i) Thermochemical considerations, performed at the B3LYP level, as well as the labeling data obtained for dehydrogenation of ethane (*Eqns. 4–7*), rule out the formation of separate C_2H_4/H_2 products; rather, intact C_2H_6 has to be regenerated in the degenerate hydrogen exchange.

ii) While the experimental findings can be modeled in terms of various scenarios⁵), due to the *ca.* 10% of scrambling, indicated by the formations of $Ni(C,H_2,D)^+$ in *Eqn. 9* and $Ni(C,H,D_2)^+$ in *Eqn. 11*, and the fact that the extent of degenerate exchange is time and pressure-dependent, we refrain from a speculative analysis of the complex data.

It will remain a challenge for future experimental/computational studies to uncover the detailed mechanistic aspects of this seemingly simple puzzle⁶).

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⁴) We mention in passing that, in addition to the exchange products shown in *Eqns. 8–11*, for some couples also isotope variants are formed which are identical with the starting $Ni(C,H_{3-x},D_x,O)^+$ complexes. Of course, their amount cannot be extracted from the data.

⁵) For example, a good fit can be obtained by assuming the following: Each methyl group of the incoming ethane molecule delivers one H-atom, which together with the three of the Ni-bound (C,H_3,O) ligand form a pool of five indistinguishable H-atoms, from which two are transferred back to the hydrocarbon fragment.

⁶) For a higly specific, interligand triple hydrogen migration in Fe^+–alkyne complexes, see [25].

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