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Ligand and Substrate Effects in Gas-Phase Reactions of NiX^+/RH Couples ($X=F$, Cl, Br, I; $R=CH_3$, C_2H_5, nC_3H_7, nC_4H_9)

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Dedicated to Professor David Milstein, Rehovot, on the occasion of his 60th birthday

Abstract: The reactions of small saturated hydrocarbons by gaseous nickel cations NiX^+ ($X=F$, Cl, Br, I) are investigated by means of electrospray ionization mass spectrometry. The halide cations are obtained from solutions of the corresponding Ni^{II} salts in water or methanol as solvents. NiF^+ is the only Ni^{II} halide complex that brings about thermal activation of methane. The branching ratios of the observed reactions with C_2H_6, C_3H_8, and nC_4H_{10} are shifted systematically by changing the nature of both the ligand X and the substrate RH. In the elimination of HX ($X=F$, Cl, Br, I), the formal oxidation state of the metal ion appears to be conserved, and the importance of this reaction channel decreases in going from NiF^+ to NiI^+. A reversed trend is observed in the losses of small closed-shell neutral molecules, that is, H_2, CH_4 and C_2H_6, which dominate the gas-phase ion chemistry of NiI^+/RH couples. Additionally, inner-sphere electron-transfer reactions take place for a few systems, that is, the delivery of hydride or methanide ions from the hydrocarbon to NiX^+ in the course of which the hydrocarbon is converted to a carbenium ion and the cationic metal complex gives rise to a neutral RNiX molecule ($R=H$, CH_3). This process gains importance with decreasing atomic number of the halides and with increasing the size of the alkane. Thus, it constitutes the major pathway in the reactions of NiF^+ with propane and *n*-butane, whereas it is not observed for any of the NiI^+/RH couples investigated. Concerning the regioselectivity of the reactions with propane and *n*-butane, heterolytic cleavage of secondary carbon–hydrogen bonds is clearly preferred compared to that of primary ones, as revealed by deuterium labeling studies. For the NiF^+/C_3H_8 couple, the selectivity of the hydride transfer is as large as 360 in favor of the secondary positions. Though smaller, large preferences for the activation of secondary C–H bonds are also operative in homolytic bond activation of RH ($R=nC_3H_7$, nC_4H_9).

Keywords: bond-activation selectivities · electron transfer · kinetic isotope effects · ligand effects · nickel

Introduction

Reactivity studies of transition-metal ions in the gas phase, and in particular aspects related to the ongoing challenge of selective activation of inert C–H and C–C bonds, have gained quite some attention in the past decades.[1] Clearly, coordination of a metal by a covalently bound ligand X affects considerably the electronic structure and can thus be used to control to some extent the efficiency and nature of the chemical transformations. Often, "all-or-nothing" effects can be induced. For example, although "naked" FeO^+ behaves as a powerful reagent for the activation of C–H and C–C bonds[1f] and also effects product isomerization during the course of an oxidation, for example, olefin → epoxide → aldehyde, the mono-ligated species $Fe(L)O^+$ ($L=$benzene, pyridine) are entirely unreactive toward bond activation of alkanes.[2] In contrast, oxygen atom transfer from $Fe(L)O^+$ to olefins (see Scheme 1) occurs at the collision rate with less than 10% formation of by-products, and—based on circumstantial evidence—formation of epoxides rather than ketones or aldehydes takes place. As the $Fe(L)O^+$ catalyst itself can be conveniently regenerated by treating $Fe(L)^+$ with N_2O, with an efficiency ranging from 40–86% depending on L, a catalytic cycle closes.[1n] Clearly, this example demonstrates that an appropriately chosen

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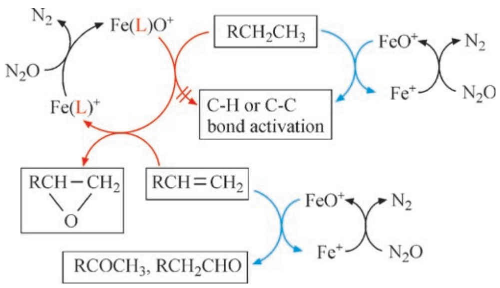


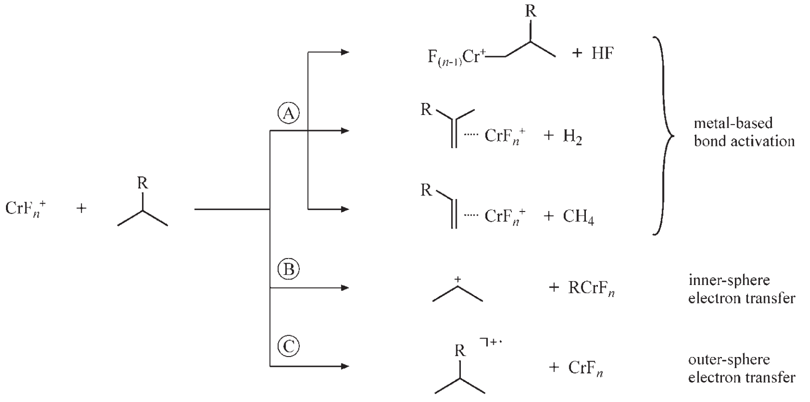
Scheme 1.

ligand can enhance the selectivity of a reagent at the expense of reactivity.[2] Interesting ligand effects have also been observed in the H^-/D^- transfer from the methyl group of labeled *N*,*N*-dimethylaniline to $Fe(L)O^+$ ($L = C_6H_6$, C_6H_5CN) such that the size of the kinetic isotope effect (KIE) could be varied by tuning the electronic properties of the ligand L.[3]

Similarly, whereas the naked cations M^+ (M = Fe, Co, Ni and Pd) do not bring about thermal C–H bond activation of methane,[1c,d] the corresponding MH^+ ions give rise to efficient H/CH_3 ligand switches [Eq. (1)]. Depending on the electronic structures of MH^+, this reaction occurs directly or is preceded by partial hydrogen-exchange processes;[4] further, the detailed mechanism of the C–H bond activation varies significantly for the Group 10 metal hydride cations MH^+ (M = Ni, Pd, Pt).[4c,f]

$$MH^+ + CH_4 \longrightarrow [MCH_3]^+ + H_2 \qquad (1)$$
$$(M = Fe, Co, Ni, Pd, Pt)$$

Similarly striking is the observation that ground-state atomic Cr^+ does not display any reactivity toward saturated hydrocarbons,[5] whereas the diatomic $CrCl^+$ reacts with alkanes larger than propane; in turn bare Fe^+ activates small alkanes, whereas $FeCl^+$ does not.[6] Further, it is not really surprising that not only the nature of the ligand X controls the outcome of a given ion–molecule reaction, as for example demonstrated in a systematic investigation of FeX^+ cations (X = H, CH_3, C_3H_5, NH_2, OH, F, Cl, Br, I) with acetone;[7] also the number of ligands as well as the substrate itself matter, and the generic reactions of CrF_n^+/alkane complexes depicted in Scheme 2 may serve as an illustrative example. Here, with both increasing oxidation state of chromium, that is, the number n of fluorine atoms attached to it, and increasing size of the alkane, the branching ratio of the possible reaction pathway shifts from homolytic C–H and C–C bond activation (path A) to hydride and methanide–ion transfer (path B) to yield carbocations, and finally to electron transfer (path C) generating hydrocarbon cation radicals.[8] Finally, in this context it is to be pointed out that in contrast to open-shell ligands X which form a covalent bond with the metal cation, coordination of closed-shell ligands L often decreases or even completely suppresses bond activation reactions;[2,9] among the few notable exceptions of ligand-*enhanced* reactivity are complexes with carbonyl ligands.[10,11]



Scheme 2.

Pronounced ligand effects and the role of formal oxidation states in metal-mediated thermal bond activation have also been reported for various cationic nickel systems.[4] As already mentioned, bare Ni^+ does not activate CH_4, whereas diatomic NiH^+ brings about ligand exchange [Eq. (1)], at temperatures as low as 80 K.[4c] Interestingly, thermochemical considerations alone are not a sufficient criterion to permit for the occurrence of these and related reactions, because for several systems with $M^+{-}X$ bond weaker than the $M^+{-}CH_3$ bond, thermal activation of CH_4 does not take place, and the Ni^{II} complexes described in Equation (2) may serve as useful examples. Although for the NiX^+ cations with X = OH, OCH_3 the X/CH_3 ligand exchanges are exothermic,[12] their non-occurrence points to the existence of kinetic barriers.[1c,l]

$$NiX^+ + CH_4 \not\longrightarrow [NiCH_3]^+ + HX \qquad (2)$$
$$(X = OH, OCH_3)$$

Higher alkanes are in general much more reactive than methane, and already C_2H_6 gives rise to efficient, mechanistically extremely puzzling dehydrogenation as well as extensive, degenerate hydrogen exchange when reacted under thermal, single-collision conditions with $Ni(C,H_3,O)^+$.[13]

Here we will describe gas-phase experiments of various NiX^+/RH couples (X = F, Cl, Br, I; R = CH_3, C_2H_5, nC_3H_7, nC_4H_9) generated and studied under the conditions of electrospray ionization (ESI) mass spectrometry. We will show that the richness of reactions previously observed by varying the formal oxidation state of the transition metal, as for example in CrF_n^+,[8] can to some extent also be achieved by systematically changing the nature of the ligand X in diatomic cations NiX^+.

Experimental Section

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.[14,15] In brief, the NiX^+ complexes were formed from millimolar solutions of NiX_2 in either methanol or water under relatively harsh ionization conditions (typical cone voltages are around 60–80 V).[16] After mass selection by means of Q1, the thermalized ions were exposed to react with the alkanes in the hexapole at room temperature and at pressures on 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;[4d,17] this provides an adequate assay of the thermal reaction rates with regard to the initial reactions.[18]

Results and Discussion

The organization of this section is such that first we will present the ion–molecule reactions for each NiX^+ complex with the four hydrocarbons employed, followed by a brief discussion of the most abundant or interesting processes. Then, for a selected class of reactant couples, labeling-experiment data are reported to trace the origin of the bonds being activated.

As a measure of the effects of X as well as the substrate RH on the reactivity of the various NiX^+/RH couples, the overall reaction rates, k_{rel}, are given in Table 1 relative to the most reactive system, that is, $NiBr^+/C_3H_8$ with $k_{rel} = 100$. The (undetected) neutral products are assigned based upon the observed mass differences Δm in conjunction with reasonable mechanistic and thermochemical considerations. In a few cases, there remain currently unresolvable ambiguities, for example, $\Delta m = 30$ may correspond either to intact C_2H_6 or to C_2H_4/H_2, and the loss of CH_5X may correspond either to HX/CH_4 or CH_3X/H_2.

In a first step, let us classify the reactions observed into three different categories: a) bond activation of the organic substrate without obvious occurrence of Ni–X bond cleavage, that is, the losses of H_2, CH_4, and C_2H_6, which formally lead to the corresponding NiX^+/olefin complexes, b) reactions involving Ni–X bond cleavage, namely the expulsions of HX, HX/H_2, and HX/CH_4, affording nickel–alkyl or nickel–alkenyl cations, respectively, and c) losses of neutral RNiX units (R = H, CH_3) concomitant with generation of the corresponding carbenium ions. Figure 1 shows the relative reaction efficiencies of channels a)–c), where the branching ratios given in Table 1 are also weighted with respect to the relative rates.

As far as general trends of the effects of the halogen ligands are concerned, activation of the alkane with maintaining the Ni–X bond intact is most effective for X = Br and I, whereas Ni–X bond cleavage is abundant for all halogens except X = I, and the formation of neutral RNiX species is of larger importance only for X = F. With regard to the size effect of the alkanes, consideration of the overall rates

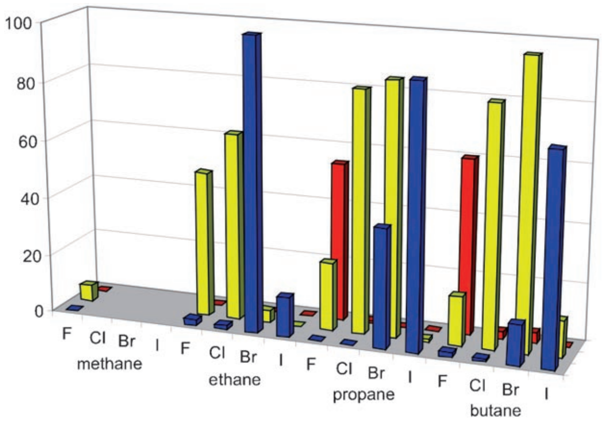


Figure 1. Relative reaction efficiencies for a) activations of the alkane without apparent cleavage of the Ni–X bond (🟦), b) reactions concomitant with Ni–X bond cleavage (🟨), and c) losses of neutral RNiX species (🟥). Here, the data from Table 1 are weighted with the relative rates and renormalized to a maximal reaction efficiency of 100 (dehydrogenation of ethane by $NiBr^+$).

Table 1. Relative rates[a] and branching ratios[b] of the neutral losses in the reactions of mass-selected NiX^+ cations (X = F, Cl, Br, I) with small alkanes R-H (R = CH_3, C_2H_5, nC_3H_7, nC_4H_9).

R	X	k_{rel}	$-H_2$	$-CH_4$	$-C_2H_6$	-HX	$-HX/H_2$	$-HX/CH_4$	-HNiX	others
CH_3	F	4				100				
	Cl	n.r.								
	Br	n.r.								
	I	n.r.								
C_2H_5	F	40	4			95	1			
	Cl	50	2			98				
	Br	80	96			4				
	I	10	100							
nC_3H_7	F	60				7	23		70	
	Cl	65				68	31		1	
	Br	100	32			50	18			
	I	70	98	1		1	<1			
nC_4H_9	F[c]	65			2	2	7	12	63	$-CH_3F$ (2), $-CH_3NiF$ (12)
	Cl[c]	65	1			3	9	84	3	
	Br	90	4	8	1	13	34	38	3	
	I	65	77[d]	6	1	8	6	1		

[a] Rates given relative to the fastest reaction observed ($NiBr^+ + C_3H_8$). [b] Normalized to a sum of 100. [c] In addition, loss of HX/C_2H_4 (or C_2H_5X) is observed (<1). [d] In addition, double dehydrogenation is observed (2 H_2, 1).

(Table 1) is quite instructive. In general, the observed trends are gradual in that most reactions occur in the same order of magnitude with the exceptions of NiF^+, which is the only nickel–halide cation capable of activating methane, and for the reaction of NiI^+ with ethane which is relatively inefficient.

A closer inspection of the reactions described in Table 1 reveals that some features are unique for a particular NiX^+/RH couple and others which several systems have in common. As mentioned, NiF^+ occupies a special position in that it brings about thermal activation of methane given in Equation (3).

$$NiF^+ + CH_4 \longrightarrow [NiCH_3]^+ + HF \tag{3}$$

Based on available experimental data,[12a,19,20] the reaction is exothermic with $\Delta_rH = -35 \pm 29\,kJ\,mol^{-1}$.[21–25] The driving force of this reaction as well as the abundant losses of either HF alone or in combination with other thermochemically favorable neutral products is provided by the exceptionally high stability of HF.[20] This way of reasoning has also been used previously to account for the reactions of, for example, FeF^+ with acetone[7] or water[26] and of $CrF_n{}^+$ with hydrocarbons,[8] water[27] or phosphanes,[28] respectively, all of which spontaneously liberate HF.

In terms of the classification made above in Scheme 2, the eliminations of the closed-shell neutral molecules HX (X = F, Cl, Br, I), H_2, CH_4, C_2H_4, and C_2H_6 (and combinations thereof) belong to reaction category A, because in these activation steps the nickel ion preserves its formal oxidation state as well as the positive charge in the reactants and products. Of course, in the various intermediates generated in a sequence of oxidative additions and reductive eliminations, the cations may well undergo several changes of their oxidation states. In the reactions of all NiX^+ ions with C_3H_8 and nC_4H_{10}, we observe cationic species of the elemental compositions $[NiC_3H_5]^+$ and $[NiC_4H_7]^+$, which most likely correspond to the well-known Ni^{II}–allyl and Ni^{II}–methylallyl complexes.

Inner-sphere electron-transfer reactions[29] (category B of Scheme 2), that is, the delivery of hydride or methanide ions from the hydrocarbon to NiX^+, are very pronounced for the NiF^+/RH couples (R = nC_3H_7, nC_4H_9), much less abundant for $NiCl^+$ and NiBr, and absent in the reactions of NiI^+ with any of the alkanes studied. Based on thermochemical considerations, for the neutral product we assign the inserted R-Ni-X structure rather than the much less stable Ni(RX) isomer (R = H, CH_3; X = F, Cl, Br). Clearly, the stabilities of the resulting carbenium ions also play a decisive role, and this channel is accordingly only observed with propane and *n*-butane which can yield secondary carbenium ions. Outer-sphere electron transfer (path C in Scheme 2) has not been observed for any of the NiX^+/RH couples studied, thus implying IE(RH) > IE(NiX).

For an elucidation of the actual C–H and C–C bonds of RH, being activated by NiX^+, we have performed ion–molecule reactions of the latter with CH_2D_2 (**1**), CH_3CD_3 (**2**), $CH_3CD_2CH_3$ (**3**), $CD_3CH_2CH_2CH_3$ (**4a**) and $CD_3CH_2CH_2CD_3$ (**4b**). Instead of discussing the rather voluminous set of experimental data in detail,[30] here we present some selected results aimed at revealing the more general trends. The discussion will centre around four subclasses of processes:

1) **Loss of HX**: Except for X = I, this elimination is observed for all NiX^+ complexes. In the unique F/CH_3 ligand switch in the reaction of NiF^+ with methane [Eq. (3)], the investigation of CH_2D_2 reveals a rather large intramolecular kinetic isotope effect of 3.3; this demonstrates that breaking of the C–H(D) and forming of the F–H(D) bonds contribute to the rate-limiting step. For ethane, the eliminations of HX and DX in the reaction with CH_3CD_3 (**2**) imply KIEs of 1.7–1.8 for all three couples NiX^+/**2** (X = F, Cl, Br), irrespective of their significantly different thermochemistry and branching ratios, that is, HX versus H_2 eliminations. For the NiX^+/C_3H_8 systems, the loss of HX exhibits a clear preference for activation of the secondary rather than the primary C–H bond of the substrate. Assuming the operation of the same KIE as obtained in the reactions with CH_3CD_3 (1.8 for NiF^+ and 1.7 for $NiCl^+$ and $NiBr^+$, respectively), the following selectivities per bond for $(C–H)_{sec}$- versus $(C–H)_{prim}$-bond activation were derived for NiX^+ in the reactions with $CH_3CD_2CH_3$ (**3**): X = F (13.6), Cl (7.8), and Br (6.9). A less pronounced selectivity prevails in the loss of HBr from the $NiBr^+$/nC_4H_{10} couple, as determined from the HBr/DBr ratio in the reaction with $CD_3CH_2CH_2CD_3$ (**4b**). After statistical correction and considering the kinetic isotope effects operative in the reaction with CH_3CD_3, the activation of a secondary versus a primary carbon–hydrogen bond of *n*-butane is favored by a factor of 4.1, and for the related system $NiCl^+$/**4b** the corresponding ratio amounts to 2.7.
   While for homolytic bond cleavages of primary versus secondary C–H bonds varying preferences have been noted previously, for example, in iron- and copper-mediated gas-phase oxygenation of propane,[31,32] the trend mentioned above for NiX^+/propane is opposite to what is usually observed for radical-based processes and also what would be expected taking into consideration only the reactivity-selectivity principle.[33]
2) **Dehydrogenation**: While for all NiX^+/RH systems studied, a combination of oxidative addition/reductive elimination steps occurs, though with varying importance, this bond-activation mode dominates the ion-molecule reactions of the couples $NiBr^+$/RH (R = C_2H_5, nC_3H_7) and NiI^+/RH (R = C_2H_5, nC_3H_7, nC_4H_9), Table 1. The investigation of the labeled substrates **2**, **3**, **4a**, and **4b** reveals several interesting mechanistic details. For example, in the reactions of NiX^+ (X = Br, I) with CH_3CD_3, dehydrogenation is preceded by extensive H/D-exchanges with KIE = 1.8 (for $NiBr^+$) and KIE = 2.6 (for NiI^+), see Equation (4).

$$\mathrm{NiX^+ + CH_3CD_3} \longrightarrow \begin{array}{lllll} & & & \mathrm{X = Br} & \mathrm{I} \\ \mathrm{[NiXC_2HD_3]^+} & + & \mathrm{H_2} & 33 & 43 \\ \mathrm{[NiXC_2H_2D_2]^+} & + & \mathrm{HD} & 57 & 51 \\ \mathrm{[NiXC_2H_3D]^+} & + & \mathrm{D_2} & 10 & 6 \end{array} \qquad (4)$$

Whereas H/D scrambling is also observed in the dehydrogenation of the homologous $\mathrm{NiX^+/C_3H_8}$ couples, there exist some subtle differences. Taking into account the respective KIEs obtained from the reactions with $\mathrm{CH_3CD_3}$ (1.8 for $\mathrm{NiBr^+}$ and 2.6 for $\mathrm{NiI^+}$), complete H/D equilibration prior to dehydrogenation of $\mathrm{CH_3CD_2CH_3}$ (**3**) would lead to the eliminations of $\mathrm{H_2/HD/D_2}$ in ratios 66:32:2 and 76:23:1 for $\mathrm{NiBr^+}$ and $\mathrm{NiI^+}$, respectively. However, based upon the high abundances of the HD loss channel in the experiments [see Eq. (5)], the amount of specific 1,2-eliminations to generate $\mathrm{NiX^+}$/propene must be rather substantial for both nickel–halide cations.

$$\mathrm{NiX^+ + CH_3CD_2CH_3} \longrightarrow \begin{array}{lllll} & & & \mathrm{X = Br} & \mathrm{I} \\ \mathrm{[NiXC_3H_4D_2]^+} & + & \mathrm{H_2} & 35 & 42 \\ \mathrm{[NiXC_3H_5D]^+} & + & \mathrm{HD} & 59 & 55 \\ \mathrm{[NiXC_3H_6]^+} & + & \mathrm{D_2} & 6 & 3 \end{array} \qquad (5)$$

Quite unexpectedly, H/D scrambling appears not to play a major role in the dehydrogenation of the $\mathrm{NiI^+}/n\mathrm{C_4H_{10}}$ couple. Rather, based on the investigations of $\mathrm{CD_3CH_2CH_2CH_3}$ (**4a**) and $\mathrm{CD_3CH_2CH_2CD_3}$ (**4b**), the labeling data, that is, $\mathrm{H_2/HD/D_2} = 93{:}7{:}0$ (for **4a**) and 82:17:1 (for **4b**), can be explained in terms of generating a mixture of 1- and 2-butene, complexed to $\mathrm{NiI^+}$, in formal 1,2-elimination reactions with a high preference for generating an internal carbon–carbon double bond.

3) **C–C Bond activation**: Here, we confine ourselves to reactions that belong to category A (Scheme 2) that is the metal ion's formal oxidation state is conserved in the course of bond activation. Further below, a C–C bond-cleavage mode involving an inner-sphere electron-transfer process (path B, Scheme 2) will be presented. As expected for C–C bond activation, the sequence of oxidative addition/reductive elimination requires a minimal chain length of the hydrocarbon, and hence is only significant for *n*-butane. Three examples deserve brief mentioning: i) In the reaction of $n\mathrm{C_4H_{10}}$ with $\mathrm{NiI^+}$, methane is liberated, and investigation of the data obtained for the isotopomers $\mathrm{CD_3CH_2CH_2CH_3}$ (**4a**) and $\mathrm{CD_3CH_2CH_2CD_3}$ (**4b**), shown in Equations (6) and (7), suggests the existence of three pathways: The majority of methane is generated via a formal 1,2-elimination; less important is a rather unusual 1,4-elimination mode, and finally, H/D scrambling contributes only to a limited extent, as indicated by the absence of $\mathrm{CH_4}$ and $\mathrm{CH_3D}$ in the $\mathrm{NiI^+}$/**4b** couple [Eq. (7)].

$$\mathrm{NiI^+ + CD_3CH_2CH_2CH_3} \longrightarrow \begin{array}{llll} \mathrm{[NiIC_3H_3D_3]^+} & + & \mathrm{CH_4} & 41 \\ \mathrm{[NiIC_3H_4D_2]^+} & + & \mathrm{CH_3D} & 7 \\ \mathrm{[NiIC_3H_5D]^+} & + & \mathrm{CH_2D_2} & 4 \\ \mathrm{[NiIC_3H_6]^+} & + & \mathrm{CHD_3} & 48 \end{array} \qquad (6)$$

$$\mathrm{NiI^+ + CD_3CH_2CH_2CD_3} \longrightarrow \begin{array}{llll} \mathrm{[NiIC_3D_6]^+} & + & \mathrm{CH_4} & 0 \\ \mathrm{[NiIC_3HD_5]^+} & + & \mathrm{CH_3D} & 0 \\ \mathrm{[NiIC_3H_2D_4]^+} & + & \mathrm{CH_2D_2} & 13 \\ \mathrm{[NiIC_3H_3D_3]^+} & + & \mathrm{CHD_3} & 81 \\ \mathrm{[NiIC_3H_4D_2]^+} & + & \mathrm{CD_4} & 6 \end{array} \qquad (7)$$

In contrast to $\mathrm{NiI^+}$, the analogous nickel(II) cations $\mathrm{NiCl^+}$ and $\mathrm{NiBr^+}$ give rise to combined eliminations of HX (X = Cl, Br) and $\mathrm{CH_4}$ in their reactions with $n\mathrm{C_4H_{10}}$. Labeling experiments are, once more, helpful in delineating the origin of the eliminated closed-shell neutral molecules although a perfectly quantitative analysis is not possible due to the fact that already the loss of HX (X = Cl, Br) involves both primary and (preferentially) secondary C–H bonds of *n*-butane (see above).

For both, $\mathrm{NiCl^+}$ and $\mathrm{NiBr^+}$ in their reactions with the two labeled *n*-butanes **4a** and **4b**, the isotope distributions are quite similar and, for the sake of brevity, here we will present only the data for $\mathrm{NiCl^+}$/**4a** and $\mathrm{NiCl^+}$/**4b** [Eq. (8) and Eq. (9)].

$$\mathrm{NiCl^+ + CD_3CH_2CH_2CH_3} \longrightarrow \begin{array}{llll} \mathrm{[NiC_3H_2D_3]^+} & + & \mathrm{[CH_5Cl]} & 4 \\ \mathrm{[NiC_3H_3D_2]^+} & + & \mathrm{[CH_4DCl]} & 46 \\ \mathrm{[NiC_3H_4D]^+} & + & \mathrm{[CH_3D_2Cl]} & 11 \\ \mathrm{[NiC_3H_5]^+} & + & \mathrm{[CH_2D_3Cl]} & 39 \end{array} \qquad (8)$$

$$\mathrm{NiCl^+ + CD_3CH_2CH_2CD_3} \longrightarrow \begin{array}{llll} \mathrm{[NiC_3D_5]^+} & + & \mathrm{[CH_4DCl]} & 1 \\ \mathrm{[NiC_3HD_4]^+} & + & \mathrm{[CH_3D_2Cl]} & 6 \\ \mathrm{[NiC_3H_2D_3]^+} & + & \mathrm{[CH_2D_3Cl]} & 22 \\ \mathrm{[NiC_3H_3D_2]^+} & + & \mathrm{[CHD_4Cl]} & 68 \\ \mathrm{[NiC_3H_4D]^+} & + & \mathrm{[CD_5Cl]} & 3 \end{array} \qquad (9)$$

An analysis of the data given in Equations (8) and (9), combined with the above discussed regioselectivities for the losses of HCl from **4a** and **4b**, suggests the following scenario. The major component corresponds to the elimination of HCl involving the secondary C–H bond of the substrate, followed by a 1,4-elimination of methane in the course of which the C(1)–C(2) bond is activated. A less important path commences with activation of a methyl C–H bond, which is completed by a formal 1,2-elimination of methane involving the other terminus of the hydrocarbon. These two "clean" channels account for most of the combined $\mathrm{HCl/CH_4}$ losses, but some product ions, for example, $\mathrm{[NiC_3H_2D_3]^+}$ from NiCl/**4b** [Eq. (9)], indicate that partial H/D scrambling precedes the actual dissociation step(s).

4) **Hydride and Methanide Transfers from RH to NiX$^+$**: All reactions so far discussed belong to category A (Scheme 2), because the metal remains charged in the reactant and product ions. A different situation is encountered, when inner-sphere electron transfer becomes possible (path B, Scheme 2) in the course of which the neutral hydrocarbon is converted to a carbenium ion; concurrently, the cationic metal complex is transferred to a neutral molecule RNiX. Predictably, the driving forces for these processes are the stability of the resulting carbenium ions and the R$^-$ affinities of NiX$^+$. While for the former there is plenty of reliable data substantiating the well-established stability order *tert.* > *sec.* > *prim.* carbocation,[34] much less is known about the thermochemistry of the resulting RNiX system, except for rather crude and—at best—qualitative guidelines. For example, one can argue that NiF$^+$ is more susceptible toward reaction with a nucleophile than, for example, NiI$^+$ simply due to the effects caused by the different electronegativities of the two ligands, etc. In short, we do not expect inner-sphere electron transfer to play an important role for substrates as small as CH_4 or C_2H_6 or for the couples containing NiI$^+$/RH. These expectations are born out by the experiments, and in the following we will focus on NiX$^+$/RH with X = F, Cl; R = nC$_3$H$_7$, nC$_4$H$_9$.

Letus begin with the methanide transfer which is exclusively observed for the NiF$^+$/nC$_4$H$_{10}$ system (Table 1). In the reaction of NiF$^+$ with the isotopologue $CD_3CH_2CH_2CH_3$ (**4a**), the two dominant processes amount to transfer of CD_3^- (52%) and CH_3^- (44%) with minor contributions of "scrambled" methanides (in total 4%). This selectivity trend is further substantiated by an overwhelmingly large transfer of CD_3 (85%) in the NiF$^+$/**4b** couple. Thus, in the course of the heterolytic C(1)–C(2) bond cleavage an intact (or nearly intact) terminal methyl group is transferred to the NiF$^+$ core. Quite likely, this reaction is coupled with facile isomerization of the nascent primary $C_3H_7^+$ cation to the substantially more stable secondary cation.

Theconceptually related hydride transfer has been observed for both NiF$^+$ and NiCl$^+$ when reacted with either C_3H_8 or nC$_4$H$_{10}$, though with only small relative abundances for the NiCl$^+$/RH systems. As to the origin of the transferred hydride species, based on the reactions with $CH_3CD_2CH_3$ and $CD_3CH_2CH_2CD_3$ and after statistical corrections for the different number of hydrogen versus deuterium atoms in the given substrates and taking into account the respective KIE values, one arrives at the following conclusions with regard to the regioselectivity of secondary versus primary heterolytic carbon–hydrogen bond cleavage: For NiF$^+$/C_3H_8 the selectivity amounts to 360 (!),[35] and for *n*-butane it is as high as 22. In the NiCl$^+$ system, the regioselectivities are somewhat smaller, but still rather impressive with figures of 62 for propane and 13 for *n*butane, favoring the cleavage of secondary carbon–hydrogen bonds.

Conclusion

The gas-phase ion-molecule reactions of ESI-generated NiX$^+$ cations (X = F, Cl, Br, I) with a set of small alkanes RH (R = H, C_2H_5, nC$_3$H$_7$, nC$_4$H$_9$) exhibit a superficially complex product spectrum. However, a qualitative analysis permits a few general trends to be extracted from the data. All reactions fall into two major categories, that is, i) metal-mediated bond activation which gives rise to the liberation of closed-shell neutral molecules (such as HX, H_2, CH_4), and ii) inner-sphere electron-transfer process in the course of which the NiX$^+$ core is converted to RNiX (R = H, CH_3) and the alkane to a carbenium ion. Outer-sphere electron transfer resulting in the formation of hydrocarbon cation radicals has not been observed in the systems studied. Although a quantitative analysis is impossible due to the lack of sufficiently reliable thermochemical data, extensive labeling experiments have helped to uncover several interesting features which shed light on aspects related to the topics of regioselective C–H and C–C bond activation, kinetic isotope effects and H/D scrambling, just to mention a few.

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[22] Preliminary calculations using the B3LYP hybrid functional[23] implemented in the Gaussian 03 program package[24] with basis sets of approximately triple-ξ quality[25] confirm this estimate by providing an exothermicity of $-63\ \mathrm{kJ\,mol^{-1}}$ for process (3). Further, the σ-metathesis like transition structure for this reaction has been located at $-19\ \mathrm{kJ\,mol^{-1}}$ relative to separated $\mathrm{NiF^+/CH_4}$.

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