FULL PAPER

Formation, Structure, and Reactivity of Gaseous $Ni_2O_2^+$

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In memoriam Chava Lifshitz

The dinuclear metal dioxide $Ni_2O_2^+$ is prepared by the reaction of gaseous Ni_2^+ with N_2O in a Fourier-transform ion-cyclotron-resonance (FT-ICR) mass spectrometer. The title compound oxidizes CO, thus proving the catalytic activity of Ni_2^+ for mediating oxygen-atom transfer from N_2O to CO. Whereas $Ni_2O_2^+$ does not react with H_2 and CH_4, it accomplishes C–H bond activation of ethane, propane, and n-

butane. In comparison to the previously studied metal-oxide clusters $Mn_2O_2^+$ and $Fe_2O_2^+$, $Ni_2O_2^+$ exhibits an enhanced reactivity, which is ascribed to a lower oxygen-binding energy.

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1. Introduction

For more than two decades, the gas-phase chemistry of diatomic transition-metal oxide cations MO^+ has been an area of active research.[1–5] The interest in these species mainly results from the fact that they are the simplest conceivable model compounds for catalytically active transition-metal oxides in the condensed phase, whose structural complexity often is prohibitive for direct mechanistic studies.

With routine methods for the generation of gaseous metal clusters at hand today,[6,7] polynuclear $M_mO_n^+$ species can be investigated as well. These cluster ions are supposed to be more realistic models for neutral, bulk transition-metal oxides than isolated MO_n^+ species, because they exhibit lower charge densities and incorporate some degree of aggregation. Nonetheless, the number of reactivity studies on $M_mO_n^+$ clusters still is limited.[8] So far, research activities have focused on $V_mO_n^+$,[9,10] their heavier homologues $Nb_mO_n^+$ and $Ta_mO_n^+$,[9] $Mn_2O_2^+$,[11] $Fe_mO_n^+$,[12,13] and Pt_mO^+.[14] In addition, reactions of the dinuclear cluster ions $Ti_2O_2^+$ and $Co_2O_2^+$ have been investigated;[15,16] however, these studies did not address the problems of C–H bond activation or oxygen-atom transfer, which are prime challenges in the context of catalysis.[17]

In the present contribution, we report on the gas-phase synthesis and reactivity of $Ni_2O_2^+$. As a group 10 element, nickel has a rather high electronegativity and is less oxophilic than earlier 3d metals. It will be interesting to see

whether the accordingly expected lower stability of $Ni_2O_2^+$, compared to the previously studied cations $Mn_2O_2^+$ and $Fe_2O_2^+$, results in an enhanced reactivity of the title compound.

2. Results and Discussion

2.1 Formation of $Ni_2O_2^+$

Ni_2^+ reacts with N_2O by oxygen-atom transfer, Equation (1). The resulting Ni_2O^+ continues to abstract oxygen from N_2O, thereby forming $Ni_2O_2^+$, Equation (2), as the final product under ICR conditions.

$$Ni_2^+ + N_2O \rightarrow Ni_2O^+ + N_2 \qquad (1)$$

$$Ni_2O^+ + N_2O \rightarrow Ni_2O_2^+ + N_2 \qquad (2)$$

The occurrence of these processes under thermal conditions implies $D_0(Ni_2^+–O) \geq D_0(N_2–O) = 161$ kJ·mol^{-1}[18] as well as $D_0(Ni_2O^+–O) \geq D_0(N_2–O)$; the first lower limit is completely in line with $D_0(Ni_2^+–O) = 457.6 \pm 3$ kJ·mol^{-1} reported by Vardhan et al.[19] Both reactions exhibit rather moderate efficiencies (Table 1). Interestingly, several mononuclear transition-metal cations M^+, including Ni^+, have been found not to react at all with N_2O at thermal energies, although oxygen transfer is allowed thermochemically.[2,20,21] The existence of barriers associated with these processes has been rationalized by spin restrictions,[22] as MO^+ correlates with atomic $O(^3P)$, whereas N_2O yields $O(^1D)$ upon adiabatic oxygen release.[2,23] Possibly, the presence of more electronic states in the Ni_2^+ cluster opens new spin-allowed reaction paths not available for the mononu-

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clear system and thus leads to the enhanced reactivity observed.

Table 1. Bimolecular rate constants k, efficiencies φ, and branching ratios (b.r.) for reactions of dinuclear nickel clusters at 298 K.

Reactants	k [cm³ s⁻¹][a]	φ	Products	b.r. (%)
$Ni_2^+ + N_2O$	3.0×10^{-11}	0.04	$Ni_2O^+ + N_2$	100[b]
$Ni_2O^+ + N_2O$	9.3×10^{-11}	0.13	$Ni_2O_2^+ + N_2$	100
$Ni_2{}^{16}O_2^+ + {}^{18}O_2$	8.0×10^{-13}	0.0015	$Ni_2{}^{16}O^{18}O^+ + {}^{16}O^{18}O$	100
$Ni_2O^+ + CO$	3.5×10^{-11}	0.050	$Ni_2^+ + CO_2$	100
$Ni_2O_2^+ + CO$	2.1×10^{-11}	0.030	$Ni_2O^+ + CO_2$	100
$Ni_2O_2^+ + C_2H_6$	1.4×10^{-10}	0.14	$Ni_2H_2O_2^+ + C_2H_4$	100
$Ni_2O_2^+ + C_3H_8$	3.8×10^{-10}	0.38	$NiC_3H_6^+ + [Ni,H_2,O_2]$	10
			$Ni_2H_2O_2^+ + C_3H_6$	90
$Ni_2O_2^+ + n\text{-}C_4H_{10}$	6.7×10^{-10}	0.64	$NiC_4H_6^+ + [Ni,H_4,O_2]$	15
			$Ni_2H_2O_2^+ + C_4H_8$	65
			$Ni_2C_4H_6^+ + 2\,H_2O$	10
			$Ni_2C_4H_8O^+ + H_2O$	10

[a] Uncertainties of the absolute rate constants estimated at 30%.[40] [b] In addition, $Ni(N_2O)^+$ is formed, see text for discussion.

In addition to oxygen-atom transfer, Ni_2^+ undergoes two side reactions. The first one yields atomic Ni^+ (ca. 7% branching ratio, b.r.) such that the neutral byproduct(s) cannot be inferred unambiguously. One possible suggestion for the latter might be NiO and N_2. According to this assignment, the formation of Ni^+ would result from spontaneous fission of part of the Ni_2O^+ clusters generated after initial O-atom transfer. For this reaction to be exothermic, the relation $D_0(Ni^+\text{–}Ni) + D_0(N_2\text{–}O) = 393 \pm 2\ \text{kJ·mol}^{-1} \leq D_0(Ni\text{–}O)$ should hold, which is consistent with the reported value $D_{298}(Ni\text{–}O) = 382 \pm 17\ \text{kJ·mol}^{-1}$ within error bars.[18] As a direct probe for the involvement of Ni_2O^+ in the generation of Ni^+, the former is subjected to a double-resonance experiment.[24] In this experiment, continuous resonant irradiation ejects all Ni_2O^+ ions formed and thus prevents the build-up of any consecutive products. The effectiveness of this measure is clearly seen from the complete removal of $Ni_2O_2^+$ upon resonant irradiation on Ni_2O^+. In contrast, the amount of Ni^+ generated is not affected, which disproves the involvement of Ni_2O^+ as its precursor, unless the dissociation of Ni_2O^+ occurs faster than the time scale of ion ejection, $\Delta_{eject}t \approx 1\ \text{ms}$. Alternatively, the formation of Ni^+ can be rationalized by reaction with residual traces of oxygen present in the high vacuum system, Equation (3). The exoergicity of this process has been demonstrated previously.[19]

$$Ni_2^+ + O_2 \rightarrow Ni^+ + NiO_2 \quad\quad\quad (3)$$

However, we cannot rigorously rule out the possible origin of Ni^+ from electronically excited reactant Ni_2^+ either. The thermochemical relations so far discussed rely on the assumption that all reactant cluster ions are in the electronic ground state. Yet, this assumption not necessarily appears valid in light of the results presented next.

The second side reaction (ca. 15% b.r.) leads to the formation of NiN_2O^+. As the abundance of this ion is not affected by continuous ejection of Ni_2O^+ in a double-resonance experiment, the former cannot be generated in a consecutive reaction of neither Ni_2O^+ (nor $Ni_2O_2^+$). Further-

more, NiN_2O^+ cannot result from a consecutive reaction of Ni^+ either because direct association processes are highly unlikely given the small size of the molecular systems under study as well as the low pressure regime of the experiments (and are observed neither for Ni_2^+, Ni_2O^+, nor $Ni_2O_2^+$). Last but not least, the temporal evolution of the abundance of NiN_2O^+ agrees with that of a primary product within the limits of the kinetic scheme applied[25] in that it appears to be formed by a formally direct exchange of Ni for N_2O, Equation (4). At longer reaction times, the yield of NiN_2O^+ declines while NiH_2O^+ emerges as new product ion. A double-resonance experiment confirms that the latter originates from the former. Because traces of water, like oxygen, are inevitably present in the vacuum system, the formation of NiH_2O^+ can obviously be rationalized by a substitution of N_2O for H_2O, Equation (5). The facile occurrence of this exchange suggests that NiN_2O^+ contains an intact N_2O ligand and the ion is thus assigned to correspond to a $Ni(N_2O)^+$ complex.[26]

$$Ni_2^+ + N_2O \rightarrow Ni(N_2O)^+ + Ni \quad\quad\quad (4)$$

$$Ni(N_2O)^+ + H_2O \rightarrow Ni(H_2O)^+ + N_2O \quad\quad\quad (5)$$
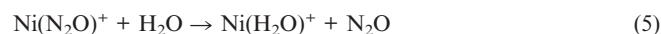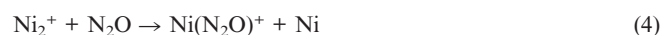
Whereas the secondary exchange reaction is substantially exothermic, $D_{298}(Ni^+\text{–}H_2O) = 184 \pm 3\ \text{kJ·mol}^{-1}$[27] vs. $D_0(Ni^+\text{–}N_2O) = 105.7 \pm 0.3\ \text{kJ·mol}^{-1}$,[28] the first one is strongly endothermic for ground-state Ni_2^+ ($D_0(Ni^+\text{–}Ni) = 204 \pm 10\ \text{kJ·mol}^{-1}$)[29] and should therefore not take place at ambient temperatures. The occurrence of this reaction may thus point to the presence of thermally not equilibrated reactants. Although the generation of electronically excited, long-lived metal clusters in a Smalley-type cluster ion source has not been reported to the best of our knowledge,[30] its involvement might be considered in the present case and warrants further investigation.

In order to assess the effect of the thermalization procedure on the reaction channel in question, the number of argon pulses applied was varied between 0 and 20. Yet, no decrease in the combined abundances of $Ni(N_2O)^+$ and $Ni(H_2O)^+$ was observed. This result is in fact not at all surprising because the Ni_2^+ ions present in the analyzer cell of the FT-ICR mass spectrometer already have undergone a large number of collisions with helium atoms in the supersonic expansion occurring in the Smalley-type cluster-ion source. If any electronically excited Ni_2^{+*} survived these conditions, it should not be quenched by collisions with argon atoms either. The absence of any reaction with argon also suggests a lower limit for the bond dissociation energy of the hypothetical excited Ni_2^{+*} cluster (if the operation of kinetic barriers is neglected), whereas the substitution of one Ni atom by N_2O according to Equation (4) yields an upper limit of $D_0(Ni^+\text{–}Ar) = 54.69 \pm 0.06 \leq D_0(Ni^+\text{–}Ni^*) \leq 105.7 \pm 0.3\ \text{kJ·mol}^{-1}$.[28,31] Ligands L stronger than N_2O then should react with Ni_2^{+*} in a similar manner to afford NiL^+ complexes. However, the nickel dimer prepared did neither react with Xe, CO, nor H_2O, although at least the latter two clearly bind Ni^+ more strongly than N_2O does [$D_0(Ni^+\text{–}CO) = 175 \pm 11\ \text{kJ·mol}^{-1}$,[29] $D_{298}(Ni^+\text{–}H_2O) = 184$
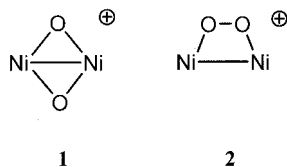
± 3 kJ·mol^{-1}].[27] Hence, these experiments do not support the generation of electronically excited, long-lived Ni$_2$$^+$ in the cluster-ion source.

An alternative explanation for the formation of Ni-(N$_2$O)$^+$ borrows from a recent study of Bohme and co-workers, in which termolecular processes were reported to account for the coupling of two or more NO$_x$ molecules by transition-metal ions.[32] With respect to the present case, a plausible scenario for the formation of Ni(N$_2$O)$^+$ would involve a reaction of ground-state Ni$_2$$^+$ with two molecules of N$_2$O to yield NiO + N$_2$ as neutral byproducts. However, the low pressures sampled in the present experiments render the occurrence of termolecular reactions highly improbable, in contrast to the conditions applied by Bohme and co-workers.[32]

None of the different suggestions discussed above achieves a conclusive explanation of all experimental findings. Possible other rationalizations include the involvement of impurities and/or fast reacting intermediates that escape attention within the kinetic limits of the ICR studies.[25] Given the low efficiency of Ni(N$_2$O)$^+$ formation (only ≈ 6 out of 1000 collisions are successful), these factors might indeed be important while difficult to probe. Additional insight could possibly be gained from the application of other mass spectrometric techniques. Note, however, that the unknown origin of NiN$_2$O$^+$ by no means affects the reactivity studies of the title compound Ni$_2$O$_2$$^+$ which are described in the next section.
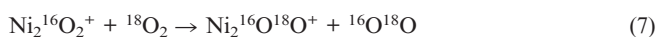
2.2 Structure and Reactivity of Ni$_2$O$_2$$^+$

The first aspect to be discussed is the structure of the Ni$_2$O$_2$$^+$ cluster formed upon reaction of Ni$_2$$^+$ with N$_2$O. Two alternatives appear most likely: The dioxide species **1** or the peroxide **2** (Scheme 1). To distinguish between these alternative structures, Ni$_2$O$_2$$^+$ is subjected to CID, which yields Ni$^+$ and Ni$_2$O$^+$ as ionic fragments, respectively (Equation 6).

$$Ni_2O_2^+ \rightarrow Ni^+ + NiO_2 \quad 85\%$$
$$Ni_2O_2^+ \rightarrow Ni_2O^+ + O \quad 15\% \qquad (6)$$

Scheme 1.

This fragmentation pattern is consistent with the parent ion having structure **1**, whereas an additional channel under expulsion of O$_2$ might be expected for a peroxide species, **2**. As a further probe, Ni$_2$O$_2$$^+$ is exposed to ^{18}O$_2$. In case of the peroxide **2**, a relatively facile exchange of the O$_2$ unit might occur. In contrast, the reaction observed experimentally is very slow (Table 1) and only brings about stepwise

^{16}O/^{18}O exchange, Equation (7). Therefore, the dioxide structure **1** is assumed most plausible for Ni$_2$O$_2$$^+$.[7,33]

$$Ni_2{}^{16}O_2^+ + {}^{18}O_2 \rightarrow Ni_2{}^{16}O^{18}O^+ + {}^{16}O^{18}O \qquad (7)$$

For an evaluation of the oxidative power of Ni$_2$O$_2$$^+$, first its reaction with carbon monoxide is studied. While the efficiency of this process is low, Ni$_2$O$_2$$^+$ indeed succeeds in the oxidation of CO, Equation (8). Moreover, the resulting Ni$_2$O$^+$ also accomplishes oxygen-atom transfer to CO, Equation (9), though even less efficiently than Ni$_2$O$_2$$^+$. The stepwise release of atomic oxygen from Ni$_2$O$_2$$^+$ is yet another piece of evidence for the dioxide structure **1** rather than that of the peroxide **2** for the ionic reactant.

$$Ni_2O_2^+ + CO \rightarrow Ni_2O^+ + CO_2 \qquad (8)$$

$$Ni_2O^+ + CO \rightarrow Ni_2^+ + CO_2 \qquad (9)$$

As N$_2$O spontaneously re-oxidizes Ni$_2$$^+$ and Ni$_2$O$^+$, gaseous Ni$_2$$^+$ in effect catalyzes the oxidation of CO by N$_2$O. Similar catalytic activities have been reported for several mononuclear transition-metal cations[1,17] as well as for anionic[8] and cationic platinum clusters.[14] In contrast to Ni$_2$O$_2$$^+$, Fe$_2O_2$$^+$ does not transfer an oxygen atom to CO. This difference is a first indication that Ni$_2$O$_2$$^+$ is a more powerful oxidant than Fe$_2$O$_2$$^+$, as already an analysis of the formal oxidation numbers of the metals would suggest. The average formal oxidation state of +2.5 adopted by the metals in M$_2$O$_2$$^+$ is energetically more favorable for iron, whereas nickel strongly prefers an oxidation state of +2 in its compounds.[34] Vann et al. also investigated the reactivity of Ni$_m$O$_n$$^+$ clusters towards NO, but could not clearly establish the occurrence of oxygen-transfer processes.[35]
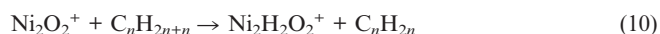
Next, Ni$_2$O$_2$$^+$ is exposed to hydrogen. From the absence of any reaction, an upper limit of $k \leq 3\times10^{-14}$ cm^3·s^{-1} can be derived which corresponds to $\varphi \leq 2\times10^{-5}$. For NiO$^+$, the reaction with H$_2$ to produce Ni$^+$ and H$_2$O does occur, but proceeds only with low efficiency although it is highly exothermic.[36] An analogous situation is encountered for the thoroughly studied system FeO$^+$ + H$_2$ where the interplay of potential-energy surfaces with different spins turns out to be crucial;[4,22] a similar importance of spin restrictions might be assumed for the reactions of NiO$^+$ and Ni$_2$O$_2$$^+$ with H$_2$. Unlike the case of oxygen transfer from N$_2$O towards Ni$^+$ vs. Ni$_2$$^+$, the transition from mononuclear NiO$^+$ to its dinuclear counterpart does not appear to weaken the effect of these spin restrictions in the particular case of H$_2$ oxidation.

The remaining reactions explored here are discussed in the context of C–H bond activation. To probe the reactivity of Ni$_2$O$_2$$^+$ in this regard, its reactions with CH$_4$, C$_2$H$_6$, C$_3$H$_8$, and n-C$_4$H$_{10}$ are considered. First insights can be gained just from inspection of the overall efficiencies observed (Table 1). While no measurable reaction takes place in the case of methane ($k \leq 1\times10^{-13}$ cm^3·s^{-1}, $\varphi \leq 1\times10^{-4}$), the efficiencies rapidly increase for the larger alkanes and closely approach unity for n-butane. This trend correlates with C–H binding energies decreasing as a function of chain length.[18] In addition, a mere size effect can be ex-
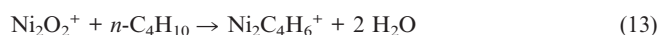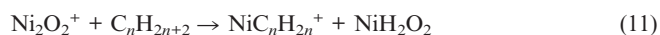
pected to further enhance the increase in reactivity. Because of their higher number of internal degrees of freedom, larger substrates can dissipate intramolecularly the energy released upon complexation more effectively and thus lower the probability for dissociation back to the reactants. For NiO^+, unity efficiency is already reached in the reaction with ethane; the increased reactivity of NiO^+ is also reflected in its ability to activate methane.[3] Attenuation of reactivity associated with the transition from mononuclear to dinuclear transition-metal oxides is a general trend also observed for manganese[11] and iron.[12,13] The lower charge densities of the cluster ions and their higher degrees of valence saturation are likely reasons for the more moderate reactivities.[37] As stated initially, exactly these properties add to their attractiveness as model compounds for real catalysts in the condensed phase.

While $Mn_2O_2^+$, $Fe_2O_2^+$, and $Ni_2O_2^+$ have in common lower reactivities towards alkanes than their mononuclear counterparts, they nonetheless also show clear differences in their efficiencies. In contrast to the moderate to high efficiencies observed for the reactions of $Ni_2O_2^+$ with C_nH_{2n+2}, n = 2–4, those reported for the reactions of $Fe_2O_2^+$ are much smaller and even in the case of n-butane do not exceed $\varphi = 0.03$.[14] With respect to $Mn_2O_2^+$, only the reaction with i-C_4H_{10} was studied, but it did not occur at a measurable rate at all.[11] Thus, $Ni_2O_2^+$ proves to be the most reactive of the $M_2O_2^+$ clusters of late $3d$ metals investigated so far.

The main product channel of the reactions of $Ni_2O_2^+$ with the alkanes studied yields $Ni_2H_2O_2^+$ and the corresponding alkene, Equation (10) with n = 2–4, thus corresponding to an oxidative dehydrogenation of the alkane. For the reduced product cluster, $Ni_2(OH)_2^+$ or Ni_2O-$(H_2O)^+$ structures seem most likely.

$$Ni_2O_2^+ + C_nH_{2n+n} \rightarrow Ni_2H_2O_2^+ + C_nH_{2n} \qquad (10)$$

In addition, mononuclear species $NiC_nH_{2n}^+$ are formed in the reactions with C_3H_8 and n-C_4H_{10}, Equation (11) with n = 3 and 4. Apparently, hydrogen transfer and complexation of the metal by the resulting alkene provide sufficient energy to cleave the Ni–Ni bond. In the case of n-C_4H_{10}, single and double dehydration occurs as well, Equation (12) and (13).

$$Ni_2O_2^+ + C_nH_{2n+2} \rightarrow NiC_nH_{2n}^+ + NiH_2O_2 \qquad (11)$$

$$Ni_2O_2^+ + n\text{-}C_4H_{10} \rightarrow Ni_2C_4H_8O^+ + H_2O \qquad (12)$$

$$Ni_2O_2^+ + n\text{-}C_4H_{10} \rightarrow Ni_2C_4H_6^+ + 2\,H_2O \qquad (13)$$

An analysis of the kinetic data as well as a double-resonance experiment show that $Ni_2C_4H_8O^+$ also results from a secondary reaction of $Ni_2H_2O_2^+$. This process combines expulsion of H_2O with dehydrogenation of the organic substrate, Equation (14), thus demonstrating an appreciable reactivity of the primary product ion $Ni_2H_2O_2^+$. In addition, this species yields $Ni_2C_4H_{10}O_2^+$ upon reaction with n-C_4H_{10}, Equation (15). While this consecutive process formally corresponds to a substitution of H_2 by n-C_4H_{10}, it is

better interpreted as a dehydrogenation of the alkane leading to a $Ni_2H_2O_2^+(C_4H_8)$ complex.

$$Ni_2H_2O_2^+ + n\text{-}C_4H_{10} \rightarrow Ni_2C_4H_8O^+ + H_2 + H_2O \qquad (14)$$

$$Ni_2H_2O_2^+ + n\text{-}C_4H_{10} \rightarrow Ni_2C_4H_{10}O_2^+ + H_2 \qquad (15)$$

In another secondary reaction with n-C_4H_{10}, $Ni_2C_4H_6^+$ forms $Ni_2C_8H_{12}^+$, Equation (16). This process is remarkable as it shows that $Ni_2C_4H_6^+$, though supposedly already binding 1,3-butadiene as a bifunctional ligand, still is capable of double dehydrogenation of n-butane.

$$Ni_2C_4H_6^+ + n\text{-}C_4H_{10} \rightarrow Ni_2C_8H_{12}^+ + 2\,H_2 \qquad (16)$$

The reactions of $Ni_2O_2^+$ with C_3H_8 and n-C_4H_{10} display several similarities compared to the processes observed for $Fe_2O_2^+$ (for the latter, no reaction products could be detected upon exposure to C_2H_6).[13] For both clusters, dehydrogenation of the alkanes yielding $M_2H_2O_2^+$ corresponds to the main reaction channel, compare Equation (10). In analogy to Equation (12), $Fe_2O_2^+$ also accomplishes dehydration of n-C_4H_{10}. Sufficiently exothermic reactions of $Fe_2O_2^+$ with larger hydrocarbons lead to the cleavage of the metallic cluster core, thereby resembling the formation of $NiC_nH_{2n}^+$ in Equation (11). However, there are also some interesting differences between the reactivities of $Ni_2O_2^+$ and $Fe_2O_2^+$. The reactions of $Fe_2O_2^+$ with n-butane and larger alkanes yield protonated alkenes, thus allowing an estimation of the proton affinity of Fe_2HO_2, $PA(Fe_2HO_2)$ ≈ 750–815 kJ·mol^{-1}.[13] From the absence of $C_4H_9^+$ in the reaction of $Ni_2O_2^+$ with n-C_4H_{10}, one could infer the inequality $PA(Ni_2HO_2) > PA(Fe_2HO_2)$ under the assumption that protonation of the resulting olefin by $Ni_2H_2O_2^+$ is prevented on thermochemical rather than kinetic grounds. Another product in the reaction of $Fe_2O_2^+$ with n-C_4H_{10} is $Fe_2C_2H_6O_2^+$,[13] whereas $Ni_2O_2^+$ exclusively reacts in terms of C–H bond activation and thus exhibits a higher selectivity than $Fe_2O_2^+$, although it is clearly more reactive in terms of the overall reaction efficiency.

3. Conclusions

The cluster cation $Ni_2O_2^+$ can be generated by a gas-phase reaction of Ni_2^+ with N_2O. Analogous procedures might also be used for the efficient preparation of other $M_2O_2^+$ species (compare ref.[12] for the case of $Fe_2O_2^+$, however), whereas most synthetic protocols reported so far directly introduce oxygen in the cluster source[15] or alternatively rely on volatile metal carbonyls.[11,13,16] Evidence is presented that $Ni_2O_2^+$ prepared by the method described here exhibits a genuine dioxide structure.

The observed reactions of $Ni_2O_2^+$ probed can be divided into two classes: Oxygen-atom transfer and C–H bond activation. The first reaction type is operative in the oxidation of CO, a process which could easily be made catalytic if N_2O were provided for the regeneration of $Ni_2O_2^+$. C–H bond activation occurs upon reaction of $Ni_2O_2^+$ with the hydrocarbons ethane, propane, and n-butane. In contrast

to its smaller homologue NiO^+, $Ni_2O_2^+$ does not activate methane, however, thus demonstrating the moderating effect of the transition from mononuclear ions to clusters. In a more general sense, this attenuation in reactivity can be considered as a closer resemblance to the behavior of transition-metal oxides in the condensed phase and thus as an improvement of the gas-phase model for applied catalysis. In comparison to $Mn_2O_2^+$ and $Fe_2O_2^+$, the reactivity of $Ni_2O_2^+$ still is remarkably high, which can be ascribed to a lowered stability of this compound with a formal oxidation state exceeding the value of +2 preferred for nickel.

Experimental Section

Experiments are performed by means of a Spectrospin CMS 47X Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer[38] equipped with a Smalley-type[6] cluster-ion source developed by Bondybey, Niedner-Schatteburg, and co-workers.[7,10] In brief, the fundamental of a pulsed Nd:YAG laser (λ = 1064 nm, Spectron Systems) is focused onto a rotating nickel target. The metal plasma thereby generated is entrained in a synchronized helium pulse (15 bar backing pressure) and cooled by supersonic expansion. After passing a skimmer, the cationic components of the molecular beam are transferred into the analyzer cell where they are trapped in the field of a 7.05 T superconducting magnet.

After mass selection of the $^{58}Ni_2^+$ cluster by means of the FERETS ion-ejection technique,[39] argon gas is pulsed-in for ion thermalization. Ni_2^+ is then exposed to N_2O at a static pressure $p \approx 3\times10^{-7}$ mbar. Based on the pseudo first-order kinetic approximation, the temporal evolution of Ni_2^+, the primary product Ni_2O^+, and the consecutive product $Ni_2O_2^+$ is compared to a fit that yields bimolecular rate constants k for both the primary and consecutive reaction with absolute errors estimated to $\pm 30\%$.[40] Reaction efficiencies $\varphi = k/k_{cap}$ are calculated according to capture theory.[41] For the reactivity studies, $Ni_2O_2^+$ is generated by pulsing N_2O to mass-selected, thermalized $^{58}Ni_2^+$ and mass-selected prior to exposure to the static neutral substrate. Bimolecular rate constants and efficiencies are derived as described for the reaction of Ni_2^+ with N_2O. Collision-induced dissociation (CID) of $Ni_2O_2^+$ is accomplished by collision of the kinetically excited ions with pulsed-in argon gas.

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