On the Origin of the Surprisingly Sluggish Redox Reaction of the $\text{N}_2\text{O}$/
CO Couple Mediated by $[\text{Y}_2\text{O}_2]^{+}$ and $[\text{YAIO}_2]^{+}$ Cluster Ions in the
Gas Phase**

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Dedicated to Professor Peter B. Armentrout on the occasion of his 60th birthday

Catalytic conversion of harmful gases produced in fossil-fuel combustion or in large-scale chemical transformations, such as CO or the oxides of nitrogen into nitrogen and carbon dioxide, is of utmost importance both environmentally and economically. For example, $\text{N}_2\text{O}$ is a potent greenhouse gas with a warming potential exceeding that of CO$_2$ by a factor of 300,[1] and its role in the depletion of stratospheric ozone is well known.[2] While these redox reactions are exothermic, for example $\Delta H = -357 \text{kJ mol}^{-1}$ for the process $\text{N}_2\text{O} + \text{CO} \rightarrow \text{N}_2 + \text{CO}_2$, they do not occur directly to any measurable extent at either room or elevated temperatures because of high energy barriers that exceed the 193 $\text{kJ mol}^{-1}$ for the $\text{N}_2\text{O}/\text{CO}$ couple. Catalysts are required to open-up new, energetically more favorable pathways,[3] and the first example of a homogeneous catalysis in the gas phase, whereby atomic transition-metal cations bring about the efficient reduction of $\text{N}_2\text{O}$ by CO, was reported in a landmark study by Kappes and Staley,[4] which was followed in the ensuing decades by numerous investigations.[5] Recently, these studies addressed more specific questions, for example, “catalyst poisoning”, and these experiments revealed remarkable effects of both the cluster size and the charge state of the catalysts.[6] For example, the active species of the $\text{Pt}^+_7$ cluster are $\text{Pt}^+_7$, $[\text{Pt}_6\text{O}_7]^+$, $[\text{Pt}_5\text{O}_7]^+$, and $[\text{Pt}_5(\text{CO})]^+$ and it has a turnover number $>500$ at room temperature. The adsorption of more than one CO molecule onto the $\text{Pt}^+_7$ cluster, however, completely quenches the catalytic activity. Thus, coverage effects for any cluster sizes can be studied at a strictly molecular level. Similarly, the concept of “single-site catalysts”,[7] the proper characterization and identification of which constitutes one of the challenges and intellectual cornerstones in contemporary catalysis, can be probed directly in gas-phase experiments with mass-selected heteronuclear metal-oxide clusters. For example, catalytic room-temperature oxidation of CO by $\text{N}_2\text{O}$ can be mediated by the bimetallic oxide cluster couple $[\text{AlVO}_4]^+|[\text{AlVO}_3]^+$. In the presence of CO, the cluster ion $[\text{AlVO}_4]^+$ is efficiently reduced to $[\text{AlVO}_3]^+$, and if $\text{N}_2\text{O}$ is added, the reverse reaction occurs. Both processes are clean and proceed with efficiencies ($\phi$) of 59% and 65%, respectively, relative to the collision rates. Most interestingly, the two redox reactions occur at the Al-O$^-$ unit of the cluster (O$: terminal oxygen atom); bond activation involving the V=O moiety cannot compete kinetically and thermochemically. Thus, the existence and operation of an “active site” of a catalyst can already be demonstrated in a rather small heteronuclear cluster.[9]

In view of the intriguing role of, for example, doping effects in the gas-phase reactions of heteronuclear cluster oxides,[9c-e,11] the investigation of the $[\text{YAIO}_3]^+/[\text{YAIO}_2]^+$ and $[\text{Y}_2\text{O}_3]^+/[\text{Y}_2\text{O}_2]^+$ couples in the context of CO/$\text{N}_2\text{O}$ conversion deemed interesting, and herein we report our rather unexpected experimental/computational findings.

As shown in Figure 1a, mass-selected, thermalized $[\text{YAIO}_3]^+$ ions can be converted by $\text{N}_2\text{O}$ into $[\text{YAIO}_2]^+$ with a bimolecular rate coefficient of $9.1 \times 10^{-12} \text{cm}^3 \text{s}^{-1} \text{molecule}^{-1}$, which amounts to $\phi = 1\%$ relative to the collision rate.[10] The by-product $[\text{YAIO}_2]^+$ arises from hydrogen-atom transfer (HAT)[11] from background impurities such as water or residual hydrocarbons. If a mixture of CO and $\text{N}_2\text{O}$ (1:19) is introduced into the reaction cell, the ion-intensity ratio $[\text{YAIO}_3]^+/[\text{YAIO}_2]^+$ decreases (Figure 1b) compared to that shown in Figure 1a. Clearly, reduction of $[\text{YAIO}_2]^+$ occurs in the presence of $\text{CO}$; thus, a full thermal catalytic cycle is in operation at room temperature. The time evolutions of the reactions of $[\text{YAIO}_3]^+$ in the presence of pure $\text{N}_2\text{O}$ and with
a mixture of CO and N₂O are shown in Figure 1a,b,c,d, respectively. Clearly, the depletion of the signal for [YAlO₂]⁺ is retarded in the presence of CO because of reduction of the transiently formed [YAlO₃]⁻ cluster ion. By fitting the experimental data of the reaction sequence [YAlO₂]⁺ + N₂O → [YAlO₃]⁻ + CO + N₂O we can estimate the bimolecular rate coefficient for the conversion [YAlO₃]⁻ → [YAlO₂]⁺ to be \( 5.3 \times 10^{-10} \text{ cm}^3 \text{s}^{-1} \text{molecule}^{-1} \) (\( \phi = 77\% \)). As a consequence of the rather low intensity of the [YAlO₃]⁻-cluster ion, generated from [YAlO₂]⁺, a direct determination of the reaction rate for the process [YAlO₂]⁺ + CO → [YAlO₂]⁺ + CO₂ was not possible.

As shown in Figure 1c, the homonuclear cluster ion [Y₂O₂]⁺ can also be oxidized by N₂O to [Y₂O₃]⁺, and the bimolecular rate coefficient amounts to \( 4.2 \times 10^{-10} \text{ cm}^3 \text{s}^{-1} \text{molecule}^{-1} \) (\( \phi = 60\% \)). However, in sharp contrast to the [YAlO₂]⁺/CO couple, reduction of [Y₂O₃]⁺ with CO does not occur at a measurable rate (Figure 1d), even at a relatively high pressure of CO (up to \( 1 \times 10^{-7} \text{ mbar} \)) and a rather long reaction time (up to 10 s).

To obtain insight into the origins of the amazingly different reactivities of the [Y₂O₃]⁺ and [YAlO₃]⁻ redox systems (\( n = 2, 3 \)) towards N₂O and CO, DFT calculations using the B3LYP functional were performed. For the heteronuclear cluster [YAlO₃]⁻, the C₃v-symmetric structure 1 (Figure 2a) corresponds to the global minimum. In 1, the spin is mainly located at the aluminum atom (0.87 \( \mu_B \)), while in the homonuclear D₂h-symmetric cluster [Y₂O₃]⁻ (9: Figure 3a), the unpaired electron is delocalized equally over the two bridging yttrium atoms. In the ion/molecule reaction of 1 with N₂O the isomers 2 and 3 are energetically accessible; the former and more stable one corresponds to an end-on coordination of N₂O to the Y atom of the cluster, while in 3 the ligand interacts with the aluminum atom. This thermochemical preference of 2 over 3 is mostly due to an electrostatic effect favoring coordination of the incoming nucleophilic N₂O ligand to the much more positively charged yttrium site of the [YAlO₃]⁻ cluster ion (Figure 4). In contrast, in the generation of 3, the interaction of N₂O with the aluminum atom is rather weak. Both isomers 2 and 3 are connected by the transition structure TS23, which is located energetically just below the entrance channel of the separated reactants (Figure 2a). Direct loss of N₂ from 2 requires an activation energy of 58 kJ mol⁻¹, relative to the entrance channel, and gives rise to [Al(µ-O₂)₂Y-O⁻]⁻ (structure not shown in Figure 2), which is 192 kJ mol⁻¹ higher in energy than the product ion [Y(µ-O₂)₂Al-O⁻]⁻ (5). Thus, it is not

**Figure 1.** Mass spectra showing the reactions of a) [YAlO₂]⁺ with pure N₂O (at a pressure of \( 1.9 \times 10^{-7} \text{ mbar} \)) after a reaction time of 8 s; b) [YAlO₂]⁺ with a 1:19 mixture of CO (at a pressure of \( 1.0 \times 10^{-7} \text{ mbar} \)) and N₂O (\( 1.9 \times 10^{-7} \text{ mbar} \)) after a reaction time of 8 s; c) [Y₂O₃]⁻ with N₂O at a pressure of \( 5.8 \times 10^{-7} \text{ mbar} \) after a reaction time of 10 s; d) [Y₂O₃]⁻ with CO at a pressure of \( 1.0 \times 10^{-7} \text{ mbar} \) after a reaction time of 5 s; e) [Y₂O₃]⁻ with CO at a pressure of \( 1.9 \times 10^{-7} \text{ mbar} \) after a reaction time of 8 s; and f) [Y₂O₃]⁻ with N₂O at a pressure of \( 5.8 \times 10^{-7} \text{ mbar} \) after a reaction time of 8 s.

**Figure 2.** Simplified potential-energy profiles for the reactions of a) [YAlO₂]⁺ with N₂O and b) [YAlO₂]⁺ with CO. The energies (given in kJ mol⁻¹) are relative to the entrance channel. Some key bond lengths are given in pm, and the Mulliken spin density values (in \( \mu_B \)) in parentheses.
As the crucial TS/3 is located only 11 kJ mol\(^{-1}\) below the entrance channel, the thermodynamically rather favored oxidation step [YAlO\(_3\)]\(^+\) + N\(_2\)O → [YAlO\(_2\)]\(^+\) + N\(_2\) is kinetically impeded, and thus results in a low reaction efficiency at room temperature. Since the computational accuracy may not be higher than 10 kJ mol\(^{-1}\),\(^{[13]}\) TS/3/4 might be relatively close to the entrance channel—in line with the experimental results.

In contrast, the exothermic reduction of [YAlO\(_2\)]\(^-\) (5) with CO is not hampered by intrinsic energy barriers. However, compared with the rather straightforward reduction of [AlVO\(_3\)]\(^-\) by CO,\(^{[10]}\) the potential-energy surface (PES) for the couple 5/CO is mechanistically more subtle with regard to the liberation of CO\(_2\) from the encounter complex 6.

A completely different scenario holds true for the homonuclear [Y\(_2\)O\(_2\)]\(^+\) cluster in its reaction with N\(_2\)O. As shown in Figure 3a, the initially formed end-on encounter complex 10 rearranges through intramolecular N\(_2\) transfer to the less-coordinated Y atom to produce 11. While direct liberation of N\(_2\) gives rise to [Y(μ-O\(_3\))\(_2\)Y\(_2\)]\(^+\) (13), this path (Figure 3b, Path I) cannot compete kinetically and thermochromically with the dissociative rearrangement proceeding through 11 → TS/11 → 12 + N\(_2\) (Figure 3b, Path II). In line with previous calculations,\(^{[14]}\) the triply oxygen-bridged, C\(_2\)-symmetric cluster 12 corresponds to the global minimum; in 12 the spin is delocalized equally over two of the three oxygen atoms of [Y(μ-O\(_3\))\(_2\)Y\(_2\)]\(^+\). For the heteronuclear [YAlO\(_2\)]\(^+\) cluster, a structure related to 12 has also been located on the PES; however, as this species is 110 kJ mol\(^{-1}\) higher in energy than 5, it is unlikely to be involved in the course of the catalytic cycle.

While the formation of [Y\(_2\)O\(_3\)]\(^-\) from [Y\(_2\)O\(_2\)]\(^+\)/N\(_2\)O is favored both kinetically and thermochromically, reduction of the former by CO is kinetically impeded by an intrinsic energy barrier (Figure 3e). Thus, in keeping with the experimental findings, despite an exothermicity of 83 kJ mol\(^{-1}\), regeneration of [Y\(_2\)O\(_3\)]\(^-\) does not take place and the catalytic cycle cannot be closed.

The distinctly different reactivity of [Y\(_2\)O\(_3\)]\(^-\) versus [YAlO\(_2\)]\(^+\) in their reactions with CO is just another example of the role spin states often play in chemical reactions.\(^{[11,15]}\) In [YAlO\(_2\)]\(^+\) (5), where the spin is located at the oxygen atom of the terminal Al-O unit, there is no need to generate a “prepared state”; consequently, the reaction is barrier-free. In contrast, in [Y\(_2\)O\(_3\)]\(^-\) (12), the spin is delocalized over two bridging oxygen atoms, thus lacking a prepared state and resulting in an energy barrier for oxygen-atom transfer.

In conclusion, the unexpectedly low catalytic activities of the structurally related cluster ions [YAlO\(_2\)]\(^+\) and [Y\(_2\)O\(_2\)]\(^-\) (\(n = 2, 3\)) in their redox reactions with N\(_2\)O/CO have entirely different kinetic origins. While all the individual redox steps fulfill the thermochemical criterion of thermal catalytic oxygen-atom transfer processes, with oxygen-atom affinities (OAs) of the clusters located between O(A(N\(_2\)) = 164 kJ mol\(^{-1}\) and O(A(CO)) = 521 kJ mol\(^{-1}\),\(^{[16]}\) it is the oxidation with N\(_2\)O that constitutes the bottleneck for the heteronuclear cluster [YAlO\(_2\)]\(^+\); in contrast, oxidation of the homonuclear cluster [Y\(_2\)O\(_2\)]\(^+\)/N\(_2\)O is possible, but reduction of [Y\(_2\)O\(_3\)]\(^-\) by CO in this system is prevented by an energy barrier. These
differences are caused by “doping” effects which can control the local charge and spin distributions in the reduction of N₂O and the oxidation of CO, respectively.²⁷ In a more general sense, the reactivities of heteronuclear oxide cluster ions, in comparison with their homonuclear counterparts, can be increased,²⁸ decreased,²⁹ not significantly affected,³⁰ or in some cases even the product distributions can be altered,³¹ and these observations highlight the potential to control chemical processes by selective cluster doping.

**Experimental and Computational Section**

All experiments were performed with a Spectropsin CMS 47X Fourier-transform ion-cyclotron resonance (FTICR) mass spectrometer equipped with an external ion source, as described elsewhere.²⁹ In brief, the cluster cations [YAlO₃]⁺ and [Y₂O₂]⁺ were generated by laser ablation of an yttrium/aluminum target (with a molar ratio of 1:1) by using a Nd:YAG laser operating at 1064 nm in the presence of 0.5% O₂ seeded in a helium carrier gas. [YAlO₃]⁺ cannot be generated directly with this experimental setup. By using a series of potentials and ion lenses, the ions were transferred into the ICR cell, which was positioned in the bore of a 7.05 T superconducting magnet. After collisional thermalization by pulses of argon (ca. 2 × 10⁻⁵ mbar), the [YAlO₃]⁺, [Y₂O₂]⁺, and [Y₂O₄]⁺ ions were mass-selected and studied with respect to their reactions by introducing the substrates N₂O or CO through a leak-valve in the ICR cell. The experimental second-order bimolecular rate coefficients at room temperature were evaluated by assuming a pseudo-first-order kinetic approximation after calibration of the measured pressure and consideration of the ion-gauge sensitivities. The bimolecular rate coefficients have an uncertainty of ±30%.³² A temperature of 298 K was assumed for the thermally isolated cluster ions.³³

The density functional theory (DFT) calculations were carried out using the Gaussian 09 program³⁴ employing the hybrid B3LYP exchange-correlation functional.³⁵ The TZVP basis sets³⁶ were used for C, N, O, and Al, and the polarized triple-ζ valence basis sets (Def2-TZVP)³⁷ were selected for Y. Geometry optimizations with full relaxation of all atoms were performed. Vibrational frequency calculations were carried out to check that the reaction intermediates have zero imaginary frequency. The energies (given in kJ mol⁻¹) were corrected by zero-point vibrational energy (ZPE) contributions. Intrinsic reaction-coordinate calculations³⁸ were performed to connect the TSs with local minima.

Received: October 24, 2012
Published online: December 6, 2012

**Keywords:** cluster ions · density functional calculations · gas-phase reactions · homogeneous catalysis · ion–molecule reactions
Schlangen, M. Lerch, M. K. Beyer, H. Schwarz, Angew. Chem. 2011, 123, 1466; Angew. Chem. Int. Ed. 2011, 50, 1430.

[19] a) K. Eller, H. Schwarz, Int. J. Mass Spectrom. Ion Processes 1989, 93, 243; b) K. Eller, W. Zummack, H. Schwarz, J. Am. Chem. Soc. 1990, 112, 621; c) M. Engeser, T. Weiske, D. Schröder, H. Schwarz, J. Phys. Chem. A 2003, 107, 2855.

[20] D. Schröder, H. Schwarz, D. E. Clemmer, Y. M. Chen, P. B. Armentrout, V. I. Baranov, D. K. Bohme, Int. J. Mass Spectrom. Ion Processes 1997, 161, 175.

[21] M. J. Frisch, et al. Gaussian09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.

[22] a) C. T. Lee, W. T. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785; b) A. D. Becke, Phys. Rev. A 1988, 38, 3098; c) A. D. Becke, J. Chem. Phys. 1993, 98, 5648.

[23] A. Schäfer, C. Huber, R. Ahlrichs, J. Chem. Phys. 1994, 100, 5829.

[24] a) D. Andrae, U. Hänßermann, M. Dolg, H. Stoll, H. Preuß, Theor. Chim. Acta 1990, 77, 123; b) F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297.

[25] a) K. Fukui, J. Phys. Chem. 1970, 74, 4161; b) K. Fukui, Acc. Chem. Res. 1981, 14, 363; c) C. Gonzalez, H. B. Schlegel, J. Chem. Phys. 1989, 90, 2154; d) C. Gonzalez, H. B. Schlegel, J. Phys. Chem. 1990, 94, 5523; e) D. G. Truhlar, M. S. Gordon, Science 1990, 249, 491.