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Chemical Reactivity on Gas-Phase Metal Clusters Driven by Blackbody Infrared Radiation**

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Dedicated to Professor Zdeněk Herman on the occasion of his 80th birthday

Abstract: *We report the observation of chemical reactions in gas-phase $Rh_n(N_2O)_m^+$ complexes driven by absorption of blackbody radiation. The experiments are performed under collision-free conditions in a Fourier transform ion cyclotron resonance mass spectrometer. Mid-infrared absorption by the molecularly adsorbed N_2O moieties promotes a small fraction of the cluster distribution sufficiently to drive the N_2O decomposition reaction, leading to the production of cluster oxides and the release of molecular nitrogen. N_2O decomposition competes with molecular desorption and the branching ratios for the two processes show marked size effects, reflecting variations in the relative barriers. The rate of decay is shown to scale approximately linearly with the number of infrared chromophores. The experimental findings are interpreted in terms of calculated infrared absorption rates assuming a sudden-death limit.*

Much of the impetus behind the study of isolated metal clusters derives from the idea that they represent tractable models for the active sites in heterogeneous catalysis.[1] Here, we report a study of entrance-channel complexes for one such important catalytic process, the decomposition of nitrous oxide on small gas-phase rhodium clusters. In ion-storage experiments under nominally collision-free (ultrahigh-vacuum, UHV) conditions, absorption of nascent blackbody infrared radiation has been used to initiate both chemical reactivity and fragmentation of gas-phase rhodium clusters with molecularly adsorbed nitrous oxide molecules.

Blackbody infrared radiative dissociation (BIRD)[2] is an established technique for investigating the thermal stability of molecules and clusters with respect to unimolecular dissociation. Species are stored for extended periods within a controlled blackbody radiation field and absorption of infrared (IR) photons ultimately leads to fragmentation. Early applications of BIRD involved hydrated molecules and ions[3] but the technique has proven especially useful in the study of gas-phase biomolecular ions.[4] These have very many IR-active vibrational modes making absorption (and thus fragmentation) efficient. For similar reasons doped water clusters are also amenable to BIRD.[5] The UHV environment and long trapping times of ion cyclotron resonance (ICR) techniques make them ideal for the study of BIRD processes where dissociation timescales of seconds are common.[5a,b,6]

The role of rhodium as a reduction catalyst in the automobile three-way catalytic converter has led to detailed studies of the reactions of nitrogen oxides with small gas-phase rhodium clusters.[7] The species investigated here, $Rh_n(N_2O)_m^+$, (small Rh_n^+ clusters with molecularly adsorbed N_2O), represent entrance-channel complexes on the potential energy surface for N_2O reduction. Previous studies by IR multiple photon dissociation spectroscopy (IR-MPD)[8] and collisional activation[9] revealed that the reactive channel [Eq. (1a)]

$$Rh_nN_2O^+ \rightarrow Rh_nO^+ + N_2 \tag{1a}$$

competes with the N_2O desorption channel [Eq. (1b)].

$$Rh_nN_2O^+ \rightarrow Rh_n^+ + N_2O \tag{1b}$$

The barriers for the two processes are apparently comparable and have been calculated for the complexes with $n = 5,6$ to be approximately 60–80 kJ mol^{-1}.[8b] Barriers of this magnitude, coupled with the presence of a strong IR chromophore, mean these clusters are susceptible to activation by the background blackbody field.

Figure 1 shows the decay in the parent ion signal of $Rh_n(N_2O)^+$ ($n = 5,6$) complexes stored in a room-temperature radiation field under virtually collision-free conditions. Only the reactive, nitrous oxide decomposition channel [Eq. (1a)] is observed in the case of $Rh_6(N_2O)^+$, whereas significant N_2O loss, through the desorption channel [Eq. (1b)], is also seen for $Rh_5(N_2O)^+$. Also shown in Figure 1 are first-order kinetic

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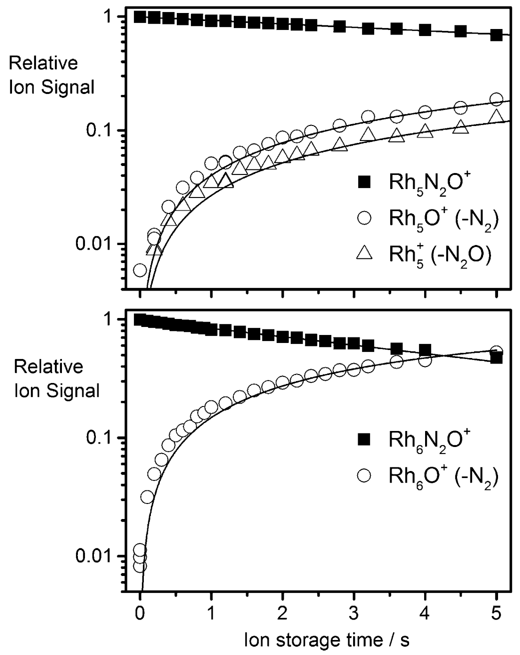

Figure 1. Decay kinetics of $Rh_nN_2O^+$ ($n = 5, 6$) clusters stored under UHV conditions ($p < 5\times10^{-10}$ mbar) in the presence of a room-temperature blackbody field. The fits (lines) assume simple first-order kinetics.

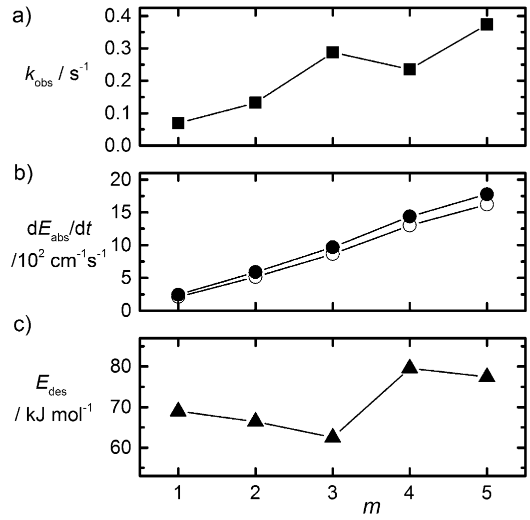

Figure 2. a) Observed decay rate constants of each $Rh_5(N_2O)_m{}^+$ species at 300 K as a function of N_2O coverage. b) Filled circles: Calculated IR absorption rates for the putative global minimum structures of $Rh_5(N_2O)_m{}^+$ obtained by convoluting the calculated IR absorption spectra with the energy density spectrum of the blackbody field. The open circles show the rate of absorption via the NO stretch only. c) Calculated N_2O desorption energies as a function of m. The anomalously low desorption energy of the third N_2O moiety accounts for the faster decay rate for this species shown in (a).

fits to the experimental data and the rate constants are given in Table S1 (see the Supporting Information, SI). A sum of two exponentials provides better fits and such modeling would be consistent with the presence of multiple isomers with differing decay rates. These effects have been reported previously for rhodium clusters[7a,b,10] but are minimal in the present case and are disregarded henceforth.

At the pressures in the ICR (ca. 5×10^{-10} mbar), collisions with background gas cannot account for the decay rates observed in Figure 1. Even assuming reaction at the collision rate of $k \approx 1\times10^{-9}$ molecule^{-1} cm^3 s^{-1}, at these pressures ions undergo collisions on average every 85 s. Furthermore, any such collisions occur at near-thermal energies (< 100 meV in the center-of-mass frame).

Instead, the processes observed result from absorption of IR radiation from the room-temperature blackbody radiation field. The N_2O moiety represents a strong mid-IR chromophore which continually exchanges photons with the background field. If, after it absorbs a photon, a reactive or dissociative process competes with emission, then the parent ion population will decay. The barriers for the processes in Equations (1a) and (1b) are sufficiently low that this is likely.

To test the notion of blackbody-driven chemistry we have performed further experiments with higher nitrous oxide coverage, $Rh_5(N_2O)_m{}^+$ ($m = 1$–5). N_2O binds preferentially at *atop* (η^1) sites, and thus $m = 5$ represents a saturation coverage. Figure 2 a) shows the observed decay rate of $Rh_5(N_2O)_m{}^+$ increasing markedly with m, consistent with this picture. This increase in decay rate with the number of chromophores is characteristic of BIRD behavior.[5e,11]

With increasing N_2O coverage, a wider variety of products is observed reflecting the increased complexity of the system. For example, we observe $Rh_5O_p{}^+$ products with $p \leq 2$ for $m = 3, 4$, and $p \leq 3$ for $m = 5$. Clearly, decomposition of the first N_2O moiety is sufficiently exothermic to trigger subsequent reaction steps on a timescale that is fast compared to the ICR detection cycle.

To further test the involvement of blackbody radiation, the whole experiment was repeated for $Rh_5N_2O^+$ at 95 K, the lowest temperature we can reach in our cooled ICR cell.[6a] A tenfold increase in the parent cluster lifetime, to more than 100 s, was observed (see SI). At such long lifetimes, the leakage of room-temperature radiation through the ends of the ICR cell and residual collisions become relevant. Hence, whilst care must be taken in interpreting this result quantitatively, the data shows unambiguously that the initial internal energy of the clusters is insufficient to induce reaction. Activation by blackbody radiation of a sufficiently high temperature is required. To make a quantitative comparison with experiment we have calculated the rate of absorption of blackbody radiation by convoluting the calculated IR spectra of the putative global-minimum structures (see SI) with the spectral energy density distribution as a function of wavenumber $\tilde{\nu}$ (in J m^{-3} per unit wavenumber) calculated at 300 K according to Planck's Law [Eq. (2)].

$$E_{\text{density}} = \frac{8\pi hc\tilde{\nu}^3}{(e^{hc\tilde{\nu}/kT} - 1)} \tag{2}$$

Coupled with the appropriate Einstein coefficient for stimulated absorption, this yields a rate of IR absorption via an active mode with intensity I/km mol^{-1} corresponding to Equation (3).

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$$\frac{dE}{dt} = \frac{8\pi hc^2\tilde{\nu}^3}{(e^{hc\tilde{\nu}/kT} - 1)}I \tag{3}$$

The results are shown in Figure 2 b) and predict a smooth monotonic increase in the absorption rate constant with the number of IR chromophores. The wavenumber and intensity of the N_2O-based normal modes are affected only slightly by the addition of subsequent N_2O molecules. Likewise, the geometric structure (isomeric form) of the cluster has no material effect on the mid-IR spectrum. The trend in the calculated absorption rate matches closely that of the observed first-order decay rate constant, with a fivefold increase in both between $m = 1$ and 5. This is powerful evidence for the involvement of blackbody radiation. Even the minor deviation from linearity in Figure 2 a) around $m = 3,4$ can be explained by the density functional theory (DFT) calculations. Figure 2 c) shows the calculated N_2O desorption energies for $Rh_5(N_2O)_m^+$ complexes. This value is anomalously low (0.65 eV) for the $m = 3$ complex and this is reflected in the high decay rate of this complex. Similarly, the barrier to removal of N_2O from $Rh_5(N_2O)_4^+$ is markedly higher (0.83 eV) than for $m = 3$. The rate-reducing effect of the higher desorption energy outweighs the rate-increasing role of the additional N_2O chromophore and $Rh_5(N_2O)_4^+$ is more stable with respect to IR-driven decay than $Rh_5(N_2O)_3^+$. Addition of a further N_2O, however, at $m = 5$, more than compensates for the increased desorption energy and $Rh_5(N_2O)_5^+$ decays faster than $Rh_5(N_2O)_3^+$.

The calculations are also useful in determining which vibrational modes are most important. Figure 3 shows the IR absorption spectrum of the lowest-energy structure of the $Rh_5(N_2O)^+$ complex calculated using DFT.[8a] The strong N_2O-based modes can clearly be distinguished around 2370 cm^{-1} (NN stretch), 1310 cm^{-1} (NO stretch), and 540 cm^{-1} (bending modes). The weaker vibrational modes associated with the rhodium cluster framework are observed below 300 cm^{-1}. The IR-MPD spectra of these complexes confirm that the simulations provide a very good representation of the experimental spectra in the region of the N_2O modes.[8] Also shown in Figure 3 is the blackbody spectral energy density distribution calculated at 300 K from Equation (2). It is clear from Figure 3 that the NN stretch cannot contribute significantly to any IR-driven process by virtue of the low number density of photons at this wavenumber. Equally, although the radiation density is high in the region of the N_2O bends and Rh–Rh modes, the small oscillator strength of these transitions limits their usefulness as IR absorbers. The NO stretch around 1300 cm^{-1}, however, represents a near-optimal combination of large transition moment in a spectral region where the radiation field is strong. The dominance of this mode in determining the rate of IR absorption is shown in Figure 2 b in which the open points represent the rate of absorption via the NO stretch. In a 300 K blackbody field, the NO stretch accounts for > 85 % of the total power absorbed.

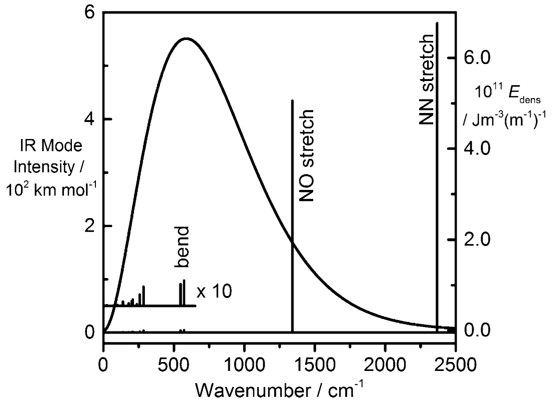

Figure 3. Calculated IR stick spectrum (scale on the left) of the putative global-minimum structure of $Rh_5N_2O^+$ (square-based pyramid with *atop*-bound N_2O) superimposed on the room-temperature blackbody radiation energy density spectrum, in J m^{-3} per unit wavenumber (solid curve, scale on the right).

In principle, any fraction of the parent cluster population which lies less than 1300 cm^{-1} below an energetic barrier can be promoted above that barrier by means of absorbing a single IR photon in the NO stretching mode. If we assume the sudden-death model of blackbody activation (applicable to small molecules, < 100 vibrational modes)[2a] in which reaction proceeds rapidly compared with radiative decay, then such an absorption process could account for our parent ion decay. This situation is illustrated schematically in Figure 4. The calculated internal energy distribution for a 300 K population of clusters is shown to scale within the entrance channel of the reactive potential energy surface. This is a hypothetical Boltzmann distribution of a cluster population that does not react. The effect of the reaction and

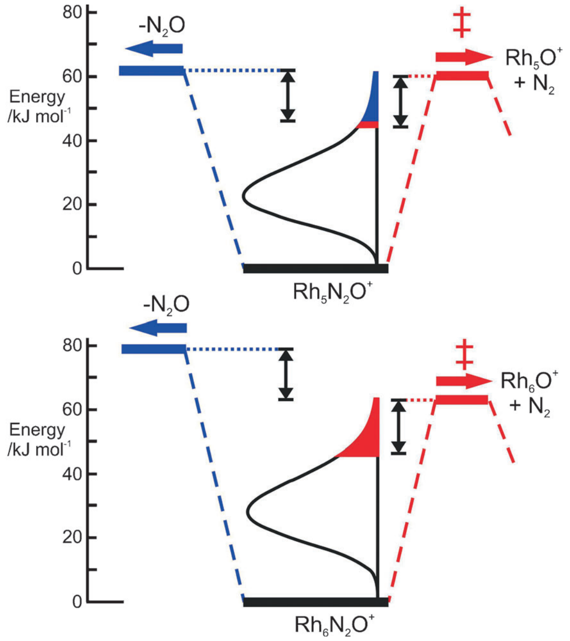

Figure 4. Calculated internal energy distributions for the entrance-channel complexes studied here (assuming 300 K), shown relative to the implied barriers for reaction (N_2 loss) and N_2O desorption. The arrows represent the energy of one quantum of the NO stretch in the N_2O moiety and thus the shaded portions of the distributions lie within one photon energy of the relevant channel opening.

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desorption channels is to truncate the actual internal energy distribution at the lowest energy threshold.[2a] The entrance channel is bound to the left by the N_2O desorption barrier and to the right by the barrier to reaction. These internal energy distributions assume the harmonic normal mode frequencies from the DFT calculations (see SI for the low-energy structures). The expectation values of the vibrational energy of these complexes at 300 K, $< E_{vib} >$, are 25.4 kJ mol^{-1} and 30.2 kJ mol^{-1}, respectively—corresponding to almost half of the likely barriers involved.

The barriers shown in Figure 4 are those implied qualitatively by the results shown in Figure 1. For $Rh_5N_2O^+$, the similar branching ratios imply that the barriers to N_2O loss and N_2O decomposition are comparable. It is equally clear that a small fraction of the parent ion distribution lies within one NO stretch quantum of this energy. Similarly, the absence of N_2O desorption from $Rh_6N_2O^+$ implies that the barrier to this process is significantly higher than that for reaction.

Blackbody activation can be compared with IR-MPD and collisional activation studies of the same complexes. In IR-MPD experiments using a free electron laser (FEL),[8] individual vibrational modes were pumped. In $Rh_5N_2O^+$, the product branching ratio was dominated by desorption with very little reaction observed. By contrast, blackbody activation leads to comparable decay rates for desorption and reaction. Reaction accounted for a larger proportion of products in IR-MPD studies of $Rh_6N_2O^+$ but was still a minor channel. Reaction is the only channel observed in the blackbody study. The explanation for these differences lies in the fluences of the excitation sources. The intensity of the FEL makes it likely that several (even many) photons are absorbed, exciting the complexes to energies at which entropic effects are important in determining reaction rates.[12] By contrast, the blackbody studies described here represent an ultimate low-fluence variant of IR excitation. The likely timescale for reaction is much shorter than the average time between photon absorptions and hence this technique provides a more sensitive probe of the relative barrier heights than does IR-MPD. The current results more closely resemble the findings from low-energy collisional activation.[9]

In summary, blackbody IR excitation has been employed to study entrance-channel complexes for the decomposition of nitrous oxide on isolated rhodium clusters. This is an unusual example of blackbody-driven chemical reactivity (as opposed to simple fragmentation) and the first we are aware of on isolated transition-metal clusters. In the chemical systems studied here, where the activation barriers are < 1 eV, this method provides a highly sensitive test of relative barrier heights in the entrance channel.

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