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

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Abstract: We report the observation of chemical reactions in gas-phase Rh₆(N₂O)₆⁺ complexes driven by absorption of black-body radiation. The experiments are performed under the collision-free, ultra high vacuum conditions in a Fourier transform ion cyclotron resonance mass spectrometer. Mid-infrared absorption by the molecularly-adsorbed N₂O moieties promotes a small fraction of the cluster distribution sufficiently to drive the N₂O decomposition reaction, leading to the production of cluster oxides and the release of molecular nitrogen. N₂O decomposition competes with molecular desorption and the branching ratios for the two processes show marked size-effects reflecting variations in the relative barriers. In experiments with varying N₂O coverage, 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 in many ways they represent tractable models for the active sites in heterogeneous catalysis.[1] Here, we report the 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 (ultra–high vacuum) conditions, absorption of nascent black–body infrared radiation has been used to initiate both chemical reactivity and fragmentation of gas–phase rhodium clusters with molecularly adsorbed nitrous oxide molecules.

Black-body infrared radiative dissociation (BIRD)[2] is a well-established technique for investigating the thermal stability of molecules and clusters with respect to unimolecular dissociation. In this method, isolated molecules or clusters are stored for extended periods within a controlled black–body radiation field. Absorption of infrared photons ultimately leads to fragmentation of the species concerned. One of the earliest applications of BIRD was to hydrated molecules and ions[3] but the technique has since proven especially useful in the study of gas-phase biomolecular ions.[4] Biomolecules typically have very many infrared–active vibrational modes making absorption (and, ultimately, fragmentation) efficient. For similar reasons doped water clusters are also highly amenable to BIRD.[5] The ultra–high vacuum environment and extended trapping times afforded by ion cyclotron resonance (ICR) techniques make them ideal for the study of BIRD processes for which dissociation timescales of seconds are common.[6, 7, 8, 9]

The role of rhodium as a reduction catalyst in the automobile three-way catalytic converter has led to detailed experimental and computational studies of the reactions of nitrogen oxides with small gas-phase rhodium clusters.[7] The species investigated here, Rh₆(N₂O)₆⁺ complexes in which N₂O is molecularly adsorbed on small Rh₆⁺ clusters, represent entrance-channel complexes on the potential energy surface for N₂O reduction.

Rh₆(N₂O)₆⁺ complexes have been studied previously both by infrared multiple photon dissociation spectroscopy (IR–MPD)[8] and by collisional activation.[9] In addition to providing valuable structural information on these complexes, these studies have revealed that the reactive channel,

\[ \text{Rh}_6\text{N}_2\text{O}^+ \rightarrow \text{Rh}_6\text{O}^+ + \text{N}_2, \]  

competes with the N₂O desorption channel,

\[ \text{Rh}_6\text{N}_2\text{O}^+ \rightarrow \text{Rh}_6^5 + \text{N}_2\text{O}, \]  

with the barriers for the two processes apparently comparable and calculated, for the \( n = 5, 6 \) complexes, to be approximately 60–80 kJ mol\(^{-1}\).[10] Barriers of this magnitude, coupled with the presence of a strong infrared chromophore, mean these clusters are susceptible to infrared activation by the background black–body field.

Figure 1 shows the decay in the parent ion signal of Rh₆(N₂O)⁺ (\( n = 5,6 \)) complexes stored in a room temperature radiation field under virtually collision–free conditions. Also shown are the only decay products observed. Under these conditions, only the reactive nitrous oxide decomposition channel (1a) is observed in the case of Rh₆(N₂O)⁶⁺, whereas significant N₂O loss, channel (1b), is also observed for Rh₆(N₂O)⁵⁺. The lines shown in Figure 1 are fits to the experimental data assuming first order decay kinetics and the extracted rate constants are given in Table S1 (see Supporting Information). Better fits can be obtained assuming a sum of two exponentials and such modelling would be consistent with the presence of multiple isomers with differing decay rates. These...
effects have been reported previously for rhodium clusters but are minimal in the present case and are disregarded henceforth.

At the background pressure in the ion storage cell (~5 × 10^{-10} mbar) the rate of collision with background gas cannot account for the decay rates observed in Figure 1. Even assuming reaction at the collision rate of \( k \approx 1 \times 10^{-6} \) molecule cm \(^{-3} \) s \(^{-1} \) (equivalent to a reaction cross section of 200 Å \(^2 \)) such as observed for reactions of \( \text{Rh}_6^{*} \) with CO, at these pressures ions undergo collisions on average every 85s. Furthermore, any such collisions with background gases occur at near-thermal energies (< 100 mV in the center of mass frame).

Instead, the processes observed result from absorption of infrared radiation from the room temperature black–body radiation field. The \( \text{N}_2\text{O} \) molecule represents a strong mid-infrared chromophore which is continually exchanging photons with the background field. If, after absorbing a photon, a reactive or dissociative process competes with emission, then the parent ion population will decay. The barriers for processes (1a) and (1b) above are sufficiently low that this is likely in \( \text{Rh}_6(\text{N}_2\text{O})^{*} \). In order to test this interpretation of black-body driven chemistry we have performed further experiments on rhodium clusters with higher nitrous oxide coverage, \( \text{Rh}_3(\text{N}_2\text{O})_m^{*} \) \( (m = 1–5) \). \( \text{N}_2\text{O} \) binds preferentially at atop (\( \psi \)) sites, and thus \( m = 5 \) represents something of a saturation coverage. The experimental results are shown in Figure 2a) and show the observed decay rate of \( \text{Rh}_3(\text{N}_2\text{O})_m^{*} \) increasing markedly with \( m \), consistent with this picture. This linear increase in decay rate with number of chromophores is characteristic of BIRD behavior.\[^{[6c, 11]}\]

With increasing \( \text{N}_2\text{O} \) coverage, a wider variety of products is observed reflecting the increased complexity of the system. For example, we observe \( \text{Rh}_3\text{O}_3^{*} \) products with \( p \leq 2 \) for \( m = 3, 4, \) and \( p \leq 3 \) for \( m = 5 \). Clearly, the decomposition of the first \( \text{N}_2\text{O} \) formation is sufficiently exothermic to trigger a second and even third reaction step on a timescale fast compared to the ICR detection cycle.

By way of further test of the involvement of blackbody radiation, we repeated the whole experiment for \( \text{Rh}_6\text{N}_2\text{O}^{*} \) at 95K, the lowest temperature we can reach in our cooled ICR cell.\[^{[8a]}\] A tenfold increase in the parent cluster lifetime, to more than 100s, was observed (see Supporting Information for the experimental data). At such long lifetimes, leakage of room-temperature radiation through the orifices at the ends of ICR cell (e.g., where the ion beam enters the cell), as well as collisions with background gas, become relevant. Care must, therefore, be taken in interpreting this result quantitatively, but this data shows unambiguously that the internal energy of the clusters which they bring from the ion source is insufficient to induce reaction. Activation by black-body radiation of a sufficiently high temperature is required. In order to make quantitative comparison with experiment we have calculated the rate of absorption of black-body radiation. This is done by convoluting the calculated IR spectra of the putative global minimum structures (see Supporting Information) with the black-body spectral energy density distribution as a function of wavenumber \( \tilde{\nu} \) \( (\text{in J m}^{-1} \text{per unit wavenumber}) \) calculated at 300 K according to Planck’s Law,

\[
E_{\text{density}} = \frac{8\pi\hbar c^3}{(e^{\hbar c / kT} - 1)}.
\]

Coupled with the appropriate Einstein \( B \) coefficient for stimulated absorption, this yields a rate of infrared energy absorbed \( \nu_{\text{IR}} \) an infrared active mode with intensity \( I / \text{km mol}^{-1} \) of

\[\frac{dE}{dt} = \frac{8\pi\hbar c^3}{(e^{\hbar c / kT} - 1)} I.
\]

The results are shown in Figure 2b). As expected, a smooth monotonic increase in the absorption rate constant with the number of IR chromophores is predicted. The wavenumber and intensity of the \( \text{N}_2\text{O} \)-based normal modes are affected only slightly by the addition of subsequent \( \text{N}_2\text{O} \) 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 that of the observed first order decay rate constant closely, with a five-fold increase in both between \( m = 1 \) and 5.

This approximately linear increase in the observed cluster decay rates of \( \text{Rh}_3(\text{N}_2\text{O})_m^{*} \) with \( m \) is powerful evidence for the involvement of black–body radiation. Even the minor deviation from linearity in Figure 2a) around \( m = 3, 4 \) can be explained by the density functional theory (DFT) calculations. Figure 2c) shows the calculated \( \text{N}_2\text{O} \) desorption energies for \( \text{Rh}_3(\text{N}_2\text{O})_m^{*} \) complexes. This value is anomalously low (0.65 eV) for the \( \text{Rh}_3(\text{N}_2\text{O})_5^{*} \) complex and this is reflected in the correspondingly high decay rate of this complex (Figure 2a). Similarly, the barrier to removal of \( \text{N}_2\text{O} \) from \( \text{Rh}_3(\text{N}_2\text{O})_5^{*} \) is markedly higher (0.83 eV) than in the neighbouring species. The rate-reducing effect of the higher desorption energy outweighs the rate-increasing effect of the additional \( \text{N}_2\text{O} \) chromophore and \( \text{Rh}_3(\text{N}_2\text{O})_5^{*} \) is correspondingly much more stable with respect to IR-driven decay than \( \text{Rh}_3(\text{N}_2\text{O})_5^{*} \). Addition of a further chromophore, however, at \( m = 5 \), more than compensates for the increased desorption energy and \( \text{Rh}_3(\text{N}_2\text{O})_5^{*} \) decays significantly faster than \( \text{Rh}_3(\text{N}_2\text{O})_4^{*} \).

The calculations are also informative in determining the important vibrational modes in these processes. Figure 3 shows the infrared absorption spectrum of the putative global minimum structure of the \( \text{Rh}_3(\text{N}_2\text{O})_4^{*} \) complex (a square-based pyramidal Rh3 structure with atop bound \( \text{N}_2\text{O} \) calculated using density functional theory.\[^{[9a]}\] The strong \( \text{N}_2\text{O} \)-based modes can clearly be distinguished around 2370 cm \(^{-1} \) (the NN stretch), 1310 cm \(^{-1} \) (the NO stretch) and 540 cm \(^{-1} \) (the 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 nitrous oxide modes.\[^{[9]}\]

Superimposed on the calculated spectrum in Figure 3 is the black–body spectral energy density distribution calculated at 300 K from equation (2). It is clear from Figure 3 that the highest frequency mode (the NN stretch) cannot contribute significantly to any IR driven process by virtue of the low number density of black-body photons at this wavenumber. Equally, although the radiation density is high in the region of the \( \text{N}_2\text{O} \) bending vibration and the vibrational modes of the metal atom framework, 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 moments 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 2b) in which the open points represent the rate of absorption via the NO stretch. In a 300K black-body field, the NO stretch accounts for >85% of the total power absorbed.

In principle then, any fraction of the parent molecule 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 black-body activation (applicable to small molecules, typically those having <100 vibrational modes\[^{[2b]}\] in which reaction proceeds rapidly compared to radiative decay, then such an absorption process could account for our parent ion decay. This situation is illustrated schematically in Figure 4 for both \( \text{Rh}_6\text{N}_2\text{O}^{*} \) and \( \text{Rh}_6\text{N}_2\text{O}^{*} \) complexes. The calculated internal energy distribution for a 300 K population of both clusters is shown to approximate
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 desorption channels is to truncate the actual internal energy distribution at the lowest energy threshold. The reaction entrance channel is bound to the left by the N\textsubscript{2}O desorption barrier and to the right by the barrier to the decomposition reaction. These internal energy distributions assume the harmonic normal mode frequencies from the DFT calculations (see Supporting Information for the low energy structures). The expectation values of the vibrational energy of these complexes at 300K, \(E_{\text{vib}}\), are 25.4 kJ mol\(^{-1}\) and 30.2 kJ mol\(^{-1}\), respectively – almost halfway up to the likely barriers involved.

The energetic barriers shown in Figure 4 are those implied qualitatively by the results shown in Figure 1. It is clear from the observed reaction products that, in the case of Rh\textsubscript{3}N\textsubscript{2}O\textsubscript{5}, the two barriers are comparable, leading to similar branching ratios for each channel. Within the model described above, it is clearly shown that some small fraction of the parent ion distribution lies within one NO stretch quantum of this energy. Likewise, the absence of any appreciable N\textsubscript{2}O desorption in the case of Rh\textsubscript{2}N\textsubscript{2}O\textsubscript{6} implies that the barrier to the decomposition reaction (N\textsubscript{2} loss channel) lies significantly below that for N\textsubscript{2}O loss.

The potential of black–body activation is demonstrated by comparison with earlier IR–MPD studies and collisional activation studies of the same complexes. In IRMPD experiments using a free electron laser (FEL), individual vibrational modes are pumped in isolation. In such studies of Rh\textsubscript{2}N\textsubscript{2}O\textsubscript{5}, the product branching ratio was dominated by the desorption process with only a very little reaction observed. By contrast, black-body IR activation leads to comparable decay rates in both desorption and reaction channels. Reaction accounted for a larger proportion of products in IRMPD of Rh\textsubscript{2}N\textsubscript{2}O\textsubscript{5} but was still a minor channel. Reaction is the only channel observed in the black–body study.

The explanation for these differences lies in the fluences of the excitation sources. The flux of the FEL used, coupled with its pulse structure, makes it likely that several (possibly many) photons are absorbed, exciting the complexes to energies at which entropic effects are important in determining reaction rates. By contrast, the black–body studies described here represent the ultimate low-fluence variant of infrared 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 IRMPD. Consistently, the results of the current black–body radiation excitation studies closely resemble the findings from our low energy collisional activation work.

In summary, black–body infrared 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 black–body 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 <1eV, this method provides a highly sensitive test of relative barrier heights in the entrance channel.

**Experimental Section**

All experiments described here were performed using a Bruker Spectrospin CMS47X Fourier–Transform ion cyclotron resonance mass spectrometer equipped with an infinity cell modified to permit close control of its temperature.\(^9\) The laser ablation cluster source used for generating transition metal clusters has been described previously.\(^9, 13\) Briefly, Rh\textsubscript{3}N\textsubscript{2}O\textsubscript{5} cluster are generated by pulsed laser ablation of a rotating rhodium disc in the presence of a pulsed helium carrier gas seeded with N\textsubscript{2}O. Clustering occurs within a narrow channel designed for this purpose. Expansion into vacuum results in a molecular beam within which a range of cluster species is entrained.

For the experiments described here, the cluster cations are accumulated in the ICR cell for 20 laser shots. Correlated frequency sweeps are then used to isolate the particular parent ion species of interest. In previous experiments, the cluster ions have been stored in the presence of either inert or reactive collision gas to investigate the effects of collisional activation.\(^9\) In the experiments described here, however, we have studied the results of interaction of the stored ions with the nascent radiation field. To this end, during the experiment, no gas is actively admitted to the ICR cell other than the trace of carrier gas which makes it all the way to the cell and a base pressure of ca. 5 \times 10\(^{-11}\) mbar is maintained. The stored ions are left to interact with the radiation field and mass spectra of the cell contents recorded as a function of storage time.

All electronic structure calculations were performed using the DFT component of the TURBOMOLE package.\(^14\) The TPS\textsuperscript{2}S\textsuperscript{15} meta-hybrid functional was used having proved reliable in reaction pathway calculations, including for this system, previously.\(^9a, \textit{b}, \textit{m} \textit{n}\) Triple-\(\zeta\) valence basis sets (def2-TZVP)\(^17\) were used for all atoms, with def2 effective core potentials for the rhodium atoms.

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Figure 1. Decay kinetics of Rh$_n$N$_2$O$^+$ (n = 5, 6) clusters stored under UHV conditions (p < 5 × 10$^{-10}$ mbar) in the presence of a room temperature black-body field. The fits (lines) assume simple first order kinetics.

Figure 2. a) Observed decay rate constants of each Rh$_n$(N$_2$O)$_m^+$ species at 300 K as a function of N$_2$O coverage. (filled points) Calculated infrared absorption rate for the putative global minimum structures of Rh$_n$(N$_2$O)$_m^+$ obtained by convoluting the calculated IR absorption spectra with the energy density spectrum of the black-body field. The open points show the rate of absorption via the NO stretch only. b) Calculated N$_2$O desorption energies as a function of m. The anomalously low desorption energy of the 3rd N$_2$O moiety accounts for the faster decay rate for this species shown in a).
Figure 3. Calculated infrared stick spectrum (left hand scale) of the putative global minimum structure of Rh₅N₂O⁺ (square–based pyramid with atop-bound N₂O) superimposed on the room temperature black-body radiation energy density spectrum, in J m⁻³ per unit wavenumber (solid curve, right hand scale).

Figure 4. Calculated internal energy distributions for the entrance channel complexes studied here (assuming 300 K), shown relative to the implied barriers for reaction (N₂ loss) and N₂O desorption. The arrows represent the energy of one quantum of the NO stretch in the N₂O moiety and thus the shaded portions of the distributions lie within one photon energy of the relevant channel opening.