Collisional activation of N₂O decomposition and CO oxidation reactions on isolated rhodium clusters

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Abstract

The reactions of nitrous oxide decorated rhodium clusters, $\text{Rh}_n\text{N}_2\text{O}^+$, ($n = 5, 6$) have been studied by Fourier transform ion cyclotron resonance mass spectrometry. Collision induced dissociation with Ar is shown to lead to one of two processes; desorption of the intact N_2O moiety (indicating molecular adsorption in the parent cluster) or N_2O decomposition liberating molecular nitrogen with the latter becoming increasingly dominant at higher collision energies. Consistent with the results of earlier studies which employed infrared excitation [Hermes *et al. J. Phys Chem Lett.* **2011**, 2, 3053], $\text{Rh}_5\text{ON}_2\text{O}^+$ is observed to behave qualitatively differently to $\text{Rh}_5\text{N}_2\text{O}^+$ with decomposition of the nitrous oxide dominating the chemistry of the former. In other experiments, the reactivity of $\text{Rh}_n\text{N}_2\text{O}^+$ clusters with CO has been studied. Chemisorption of ^{13}CO is calculated to deposit *ca.* 2 eV into the parent cluster, initiating a range of chemical processes on the cluster surface which are fit to a simple reaction mechanism. Clear differences are again observed in the reaction branching ratios for $\text{Rh}_5\text{N}_2\text{O}^+$ and $\text{Rh}_6\text{N}_2\text{O}^+$ parent cluster ions. For the $n=5$ cluster, the combined N_2O reduction / CO oxidation is the most significant reaction channel, while the $n=6$ cluster preferentially is oxidized to Rh_6O^+ with loss of N_2 and CO. Even larger differences are observed in the reactions of the N_2O decorated cluster oxides, $\text{Rh}_n\text{ON}_2\text{O}^+$ for which more reaction possibilities arise. The results of all studies are discussed in relation to infra-red driven processes on the same parent cluster species [Hamilton, S.M. *et al. J. Am. Chem. Soc.*, **2010**, 132, 1448; *J. Phys. Chem. A*, **2011**, 115, 2489].

A. Introduction

Isolated metal clusters in the gas phase provide a unique environment in which to study many of the key features of chemical reactivity free from the complexity arising from solvation or interaction with a supporting substrate.^{1, 2} With no long-range order and multiple structural forms, small clusters in many ways are ideal model systems for the surface defects which provide the active sites for interesting chemistry on extended surfaces.³⁻⁵

Quite apart from any relevance to practical chemistry, small clusters of transition metal atoms in particular present a significant challenge to modern quantum chemical calculations, especially density functional theory. Arguably, only in the last decade, with the advent of far infrared multiple photon dissociation spectroscopy using free electron lasers, has hard spectroscopic data on naked metal clusters been available against which it is possible to benchmark the results of DFT simulations.⁶⁻⁸ In many cases agreement with experiment, in the form of infrared spectra, is impressive.^{8, 9} However, in other systems, especially those involving high spin states, agreement is less convincing, with results strongly dependent on the exchange correlation functional employed and, in particular, the fraction of exact (Hartree-Fock) exchange included.^{10, 11} This type of comparison is essential if metal clusters are to live up to their billing as experimentally and computationally tractable model systems for catalytic processes.^{1, 2, 12}

The monoisotopic nature of rhodium has long made it a favourite in experimental cluster science in which mass spectrometric methods are often employed to explore size effects. In reactivity studies of charged Rh_n clusters under single collision conditions, two distinct classes of reactions have emerged. Reactions with CO ,¹³ benzene,¹⁴ azidoacetonitrile¹⁵ and NO ^{16, 17} proceed at close to collision rate and exhibit smooth, almost monotonic increases in the reaction rate constants with cluster size. By contrast, the reactions of Rh_n^+ with small alkanes^{18, 19} and nitrous oxide²⁰ are characterised by markedly slower rates and by dramatic variations in

reactivity with cluster size. The observation that the same cluster sizes, notably, Rh_n^+ $n = 5, 17-19$ and 28 display comparative unreactivity towards both alkanes and N_2O suggests such inertness is an inherent feature of these particular rhodium cluster sizes. The $\text{Rh}_n^{+/-} + \text{N}_2\text{O}$ reaction is also one (in addition to $\text{Rh}_n^+ + \text{NO}$)^{16, 17, 21} in which unusual reaction kinetics for some cluster sizes (notably cationic $n = 6-8, 11, 12$ and the $n = 8$ anionic cluster) have been interpreted in terms of the coexistence of multiple low-lying isomers with markedly different reactivity.²⁰ Such results hint at subtle effects of geometrical structure in reactivity reminiscent of the role played by defect sites in determining the chemistry of extended surfaces.³

Some of us have recently studied nitrous oxide reduction on rhodium clusters using a variant of the infrared multiple photon dissociation (IR-MPD) spectroscopy technique which has proved so successful in recent years in determining the structures of small clusters of transition metals including rhodium.^{7, 10, 11} N_2O was molecularly adsorbed on small, isolated Rh_n^+ ($n = 4-8$) clusters, and subsequently used as an infrared chromophore by which to heat the $\text{Rh}_n\text{N}_2\text{O}^+$ complex initiating a range of chemical processes on the cluster surface.^{22, 23} N_2O decomposition, resulting in N_2 loss and the formation of simple oxide clusters, was shown to compete effectively with N_2O desorption for most rhodium cluster sizes. The experimental findings were consistent with DFT calculations of the reaction pathways which predict comparable barriers for the two processes. Furthermore, computation was able to account for the anomalous reactivity of $\text{Rh}_5\text{N}_2\text{O}^+$ and $\text{Rh}_5\text{ON}_2\text{O}^+$: Uniquely in the cluster size range studied, $\text{Rh}_5\text{N}_2\text{O}^+$ proved inefficient in reducing surface-bound N_2O following infrared excitation with N_2O loss the dominant decay channel. By contrast, pumping either the N_2O or Rh-O vibrational modes of $\text{Rh}_5\text{ON}_2\text{O}^+$ leads to very efficient Rh_5O_2^+ production.²⁴ The origin of this anomaly lies in a cooperative binding effect in the case of the $\text{Rh}_5\text{ON}_2\text{O}^+$ which results in a significant increase in the N_2O binding energy (which is 0.4 eV higher on Rh_5O^+ than on Rh_5^+). As a result, upon infrared heating of $\text{Rh}_5\text{ON}_2\text{O}^+$, the reaction channel opens earlier than the N_2O loss channel.

Collision induced dissociation (CID) is a well established technique for the study of fragmentation processes in clusters. Guided ion beam variants, in particular, are effective in determining fragmentation thresholds and cross-sections both for naked metal clusters and for ligand-decorated species.^{25,26} In turn, bond dissociation energies may be determined by fitting these cross-sections²⁷ and cluster structures interpreted.¹ The extent of fragmentation as a function of collision energy has long been used to extract kinetic parameters and energy barriers for various fragmentation processes.²⁸ Here we report the results of collisional studies of the $\text{Rh}_n\text{N}_2\text{O}^+$ system performed to compare with the photoexcitation studies described above. Two conceptually different studies have been performed: Firstly, the effects of multiple collisions with an inert collision partner (argon atoms) have been studied in CID experiments at differing centre of mass collision energies. Secondly, in an attempt to better quantify the increase in internal energy of the cluster arising from a single collision, and at the same time to gain insight into the CO oxidation process, we have studied the effects of reactive collisions involving the molecular chemisorption of CO molecules onto the parent cluster.

B. Experimental

The metal cluster instrument used for all experiments reported here has been described in detail previously.^{29,30} Rhodium-containing clusters are generated by laser ablation of a rotating rhodium foil in the presence of a pulsed carrier gas. In order to generate the $\text{Rh}_n\text{N}_2\text{O}^+$ species of interest, the helium carrier gas is seeded with nitrous oxide ($<0.1\%$) and expanded from a 20 bar backing pressure *via* a piezo-operated valve. Cooling and clustering occurs in a narrow cluster channel prior to expansion into high vacuum which creates a molecular beam within which a range of cluster species are entrained.

Cationic clusters within the cluster beam are transferred via a range of ion optics to an infinity cell at the heart of a Bruker Spectrospin CMS47X FT-ICR mass spectrometer equipped with a 4.7T superconducting magnet. Figure 1 shows the mass spectrum of cationic species produced in the region of the Rh_n^+ ($n= 5,6$) cluster size range upon which this work has concentrated. A wide range of naked (Rh_n^+), oxide (Rh_nO_m^+) and nitrous oxide decorated ($\text{Rh}_n(\text{N}_2\text{O})_x^+$) clusters are produced, the relative abundances of which may be tuned with coarse control *via* parameters such as the partial pressure of N_2O , the overall backing pressure and the relative timings of the gas pulse, ablation laser firing and the ICR cell opening time. In all experiments described below, correlated frequency sweeps are used to isolate the parent cluster ion of interest. This isolation is essential in the experiments described below in order to distinguish collision- (or reaction-) induced fragmentation products from similar species within the parent ion distribution.

Collision gas and/or reactant gas is continually admitted to the ICR cell via a leak valve in order to maintain stable pressures in the region $5.0 \times 10^{-10} - 5.0 \times 10^{-8}$ mbar which is significantly above the measured background pressure in the ICR cell of $2.0 \pm 0.5 \times 10^{-10}$ mbar. All operating

pressures quoted below have been corrected for the instrumental geometry factor which accounts for the relative positions of the ICR cell and the pressure gauge,³¹ and for the sensitivity of the pressure gauge towards the gases used.³²

Two conceptually different collision experiments have been performed:

B 1. Collision Induced Dissociation of $\text{Rh}_n\text{N}_2\text{O}^+$ with Argon

The effect of collision induced dissociation with inert colliders is explored by filling the ICR cell to 2×10^{-8} mbar with argon. At these pressures parent ion fragmentation occurs on a convenient (~ 1 s) time scale. Mass-selected parent ions are excited to varying laboratory frame kinetic energies within the ICR cell with resonant excitation pulses ($V_{pp} = 17.1$ V, fixed) of differing duration, t_{exc} . Neglecting any (small) initial cyclotron motion, ions thus excited achieve lab frame cyclotron orbit speed, v_{exc} , of:³³⁻³⁸

$$v_{exc} = \frac{qV_{pp}t_{exc}G}{2md} \quad (1)$$

in which m/q is the mass-to-charge ratio of the excited ion, G is the geometry factor (0.9 for the infinity cell used here)³⁹ and d is the diameter of the ICR cell (= 60 mm). By way of example, $\text{Rh}_5\text{N}_2\text{O}^+$ ($m/q = 5.79 \times 10^{-6}$ kg C⁻¹), excited for $t_{ex} = 50$ μ s (900 μ s) results in total centre-of-mass collision energies (for collision with an argon atom) of 0.24eV (76.4 eV). These values represent the maximum available energies for the first Ar collision. Subsequent collisions will, necessarily, be of lower energy. Longer excitation times result in ions escaping the ICR cell. Following excitation, parent ions are left to undergo collisions with argon for 1.0 s after which the mass spectrum of ICR cell contents is recorded.

B 2. CO chemisorption experiments

In order to better quantify the effects of depositing a known energy into the cluster, a second series of experiments was performed in which the chemisorption of ^{13}CO to the cluster surface is used to raise the energy of the cluster species. Calculations indicate that ^{13}CO adsorption on $\text{Rh}_n\text{N}_2\text{O}^+$ is exothermic by *ca.* 1.7 eV (see details of calculations below), raising the energy of the parent cluster well above the reaction barriers to N_2O decomposition and N_2O desorption. Experiments are performed at CO cell pressures of *ca.* 2.6×10^{-8} mbar and mass spectra recorded as a function of (reaction) time. The rate constants for the CO chemisorption on bare Rh_n^+ clusters has been measured previously,^{40,13} and permit an estimate of the reactive collision rate of 0.13 s^{-1} for Rh_5^+ , and 0.38 s^{-1} for Rh_6^+ at the pressures used here. Collision rates for $\text{Rh}_n\text{N}_2\text{O}^+$ are expected to be somewhat larger. ^{13}CO was used in these experiments to avoid confusion in the interpretation of data arising from $\text{N}_2:\text{CO}$ and $\text{N}_2\text{O}:\text{OCO}$ mass coincidences.

B 3. Computational details

In support of the experimental data, the binding energies of CO to Rh_n^+ , Rh_nO^+ and $\text{Rh}_n\text{N}_2\text{O}^+$ have been calculated with density functional theory as implemented in the Turbomole v6.1 package.⁴¹ The TPSSh exchange-correlation functional⁴² was used throughout, having performed well in combined spectroscopic and reactivity studies of $\text{Rh}_n\text{N}_2\text{O}^+$.²²⁻²⁴ Triple- ζ basis sets (def2-TZVP)⁴³ were employed for all atoms with def2-ecp effective core potentials for the rhodium atoms. The starting points for all geometry optimisations were the structures of Rh_n^+ ,^{10,22} Rh_nO^+ ,⁴⁴ and $\text{Rh}_n\text{N}_2\text{O}^+$,^{23, 24} previously reported, for which some supporting spectral information exists.¹¹

C. Results and Discussion

C 1. Collision induced dissociation of $\text{Rh}_n\text{N}_2\text{O}^+$ with argon

Figure 2 shows the effects of Ar CID on the $\text{Rh}_5\text{N}_2\text{O}^+$ parent ion at two different centre of mass collision energies. The effect of the excitation pulse is clearly observed in the enhanced intensity of the daughter ion peaks at $M^+ - 44\text{u}$ (the N_2O loss, or *desorption* channel) and $M^+ - 28\text{u}$ (corresponding to N_2 loss; the *surface reaction* channel). Figure 3 shows the evolution of the parent and product ion signals as a function of centre of mass collision energy (as calculated from eqn (1)) for $\text{Rh}_n\text{N}_2\text{O}^+$ ($n=5,6$) and $\text{Rh}_n\text{ON}_2\text{O}^+$ ($n=5,6$) parent ions.

From the data in Figure 3, a number of conclusions may be drawn. Firstly, the observation of an N_2O loss channel provides evidence that nitrous oxide is molecularly bound on the surface of the rhodium cluster. This is consistent with the IRMPD experiments (in which the N_2O vibrational modes were observed) as are the trends in the branching ratios for the various fragmentation channels in each system.²²⁻²⁴

For both $n=5, 6$ clusters, the presence of a co-adsorbed oxygen atom increases the branching ratio of the N_2O decomposition reaction. This effect is most noticeable in the case of $n = 5$ for which the presence of the oxygen atom reverses the relative branching ratios for desorption and surface reaction with N_2O decomposition favoured at all collision energies on the oxide cluster. Similar observations were made in the infra-red driven studies where they were interpreted as resulting from a cooperative binding effect: Calculations indicate that the N_2O desorption energy is 0.45 eV (or >60%) higher on the oxide cluster than the naked Rh_5^+ with the result that the reactive channel opens at lower energy than the N_2O loss channel.²⁴

For all parent ions studied, the branching ratio for N_2O desorption increases with increasing collision energy. This may be interpreted as an entropic effect favouring desorption once the enthalpic barriers to both desorption and reaction are exceeded.

It is clear from Figure 3 that, even without resonant excitation, some fragmentation occurs during the 1s delay. This is manifest in the presence of significant fragmentation products at $E_{cm} = 0$. It is possible that this signal results from imperfect ejection of the relevant masses but the absence of other mass peaks would suggest otherwise. Alternatively, during the 1st second sufficient thermal collisions with Ar may occur to induce fragmentation.

A degree of care must be taken in interpreting the above measurements quantitatively because, in addition to the nominal collision energy increasing with the duration of the excitation pulse, the mean number of collisions, $\langle N \rangle$, also increases. With calculated estimates of the hard-sphere collision cross-sections from the DFT calculations of the relevant structures, we estimate that $\langle N \rangle$ varies from *ca.* 0.23 at $E_{cm} = 1$ eV to around 2.0 at $E_{cm} = 80$ eV. Furthermore, although the centre of mass collision energy may be estimated, the fraction of this energy which is deposited within the internal (vibrational) degrees of freedom of the cluster is unknown. Muntean and Armentrout considered the latter problem in collisions of $\text{Cr}(\text{CO})_6^+$ with Xe and developed a simple empirical model for estimating the distribution of deposited energy as a function of collision energy.⁴⁵ Such treatments, though, require information on the collision energy dependence of the cross-section which is unavailable here. In studies of neutral clusters, Hase *et al.* have shown that molecular dynamics simulations can yield similar information²⁴ and such a study would be informative in the case of the systems studied here.

C 2. CO chemisorption experiments

CO molecularly chemisorbs on transition metal clusters at rates close to collision rate.^{13, 40} The chemisorption (CO binding) energy which this imparts to the cluster may be estimated from DFT calculations, as shown in Table 1. These show binding energies of *ca.* 2.3 eV on $\text{Rh}_5\text{N}_2\text{O}^+$ and 1.9eV on $\text{Rh}_6\text{N}_2\text{O}^+$. On most clusters DFT calculations predict CO to bind preferentially in μ^3 hollow sites. However, IR–MPD spectroscopy experiments by Fielicke *et al.*^{46, 47} have shows convincingly that CO binds atop (μ^1) on Rh_nCO^+ for $n = 5, 6$. This tendency of DFT calculations to favour high-coordination sites on metal surfaces is a known problem.⁴⁸ Fortunately, the chemisorption energies are comparable for all binding sites, and importantly, are always substantially larger than the calculated barriers to N_2O desorption and/or decomposition. Hence, under single collision conditions, we know the energy deposited into the cluster.

The price paid for this better knowledge of the energetics is the introduction of another reactant to the surface of the metal cluster which significantly complicates the chemistry. Figure 4 shows the evolution of the $\text{Rh}_5\text{N}_2\text{O}^+$ and $\text{Rh}_6\text{N}_2\text{O}^+$ signals following 10s exposure to low pressure ^{13}CO . In order to better understand the various surface chemical processes involved, we have fit the kinetics of the CO reaction data to the simplest mechanism which accounts for all observed products:

Primary reactions:

Secondary reactions:

Even at the $\sim 3 \times 10^{-8}$ mbar pressures used here, ^{13}CO is in huge excess and each step in the mechanism can be simplified to a pseudo first order reaction with corresponding pseudo first order rate constant, k_i , as shown. We have not included the possibility of unreactive collisions driving fragmentation as, based on the results of earlier FT-ICR studies of naked $\text{Rh}_n^{+/-}$, we expect CO chemisorption to occur at close to collision rate.⁴⁰

One particular species conspicuous by its absence from this mechanism is Rh_nOCO^+ , which was not observed in any of these experiments. It seems that whenever N_2O decomposes on the surface, the resulting N_2 loss is always accompanied by CO or CO_2 desorption.

At the working CO pressures of 2.6×10^{-8} mbar we estimate the collision rate using ADO theory⁴⁹ to be $\sim 0.4 \text{ s}^{-1}$. These pressures are sufficiently low that true three-body collisions are negligible but we cannot exclude “sticky collisions” in which the collision/adsorption energy is accommodated amongst the internal vibrational degrees of freedom long enough for either a subsequent collision to remove the excess or radiative cooling to occur.

The kinetics observed for each parent ion studied here show individual features which merits their discussion separately.

C 2.1 CO chemisorption on $\text{Rh}_5\text{N}_2\text{O}^+$

Figure 5 shows the dependence on reaction time of the parent and reaction product (Rh_5^+ , Rh_5O^+ and Rh_5CO^+) signals following exposure of $\text{Rh}_5\text{N}_2\text{O}^+$ clusters to 2.6×10^{-8} mbar ^{13}CO . Clear curvature is observed in the decay of the parent ion signal with time and it cannot thus be satisfactorily fit by a single rate constant. Such kinetics are not unusual for rhodium clusters and previous studies of the reactions of rhodium clusters with small molecules have interpreted similar decay dynamics of the parent ion signal in terms of the co-existence of multiple structural isomers with differing reactivities.^{16, 17, 20, 21} Simulations predict several low-lying structures of $\text{Rh}_5\text{N}_2\text{O}^+$,²³ and many possible candidates for structural isomerism are plausible, both in the shape of the Rh_5^+ skeleton and in the binding sites of CO and N_2O . Hence, in our fitting of this data we have allowed for the possibility of two isomers of the parent. Rh_5^+ and Rh_5O^+ are both satisfactorily fit as primary products within the above mechanism with respective pseudo first order rate constants given in Table 2.

The Rh_5^+ product cannot arise as a result of CO chemisorption induced N_2O desorption as this would leave bound CO. Instead, the Rh_5^+ product is a signature of the decomposition of the N_2O moiety. Once a CO molecule adsorbs, surface decomposition of the N_2O is triggered and an N_2 molecule evolves. The exothermicity of this surface reaction is sufficient to either i) desorb the CO molecule, resulting in the oxide product, Rh_5O^+ , or ii) initiate a secondary $\text{O} + \text{CO}$ reaction on the cluster surface generating CO_2 which also desorbs leaving the naked Rh_5^+ product. DFT calculations indicate a CO_2 binding energy to Rh_5^+ of only about 0.3 eV, meaning that its desorption is eminently feasible. The efficacy of the CO oxidation reaction was tested by isolating Rh_nO^+ and exposing it to ^{13}CO atmosphere. For both $n = 5$ and $n = 6$ the dominant product was the bare Rh_n^+ cluster. This type of CO oxidation on transition metal clusters has precedent, having been observed following infrared heating of isolated $\text{Pt}_n\text{O}_m\text{CO}^+$ clusters as well as in collisional studies of platinum clusters with N_2O and CO.⁵⁰⁻⁵⁵

It proved impossible to fit the Rh_5CO^+ reaction product as a primary product arising from a straightforward CO/ N_2O displacement reaction (k_1). Given the relative binding energies of CO and N_2O such a reaction channel is clearly energetically feasible and thus it must be that the decomposition reaction is considerably faster. If so, this might suggest another cooperative binding effect as desorption dominates the dynamics of infrared heated $\text{Rh}_5\text{N}_2\text{O}^+$.²⁴ However, preliminary calculations find the N_2O binding energy to be only 0.1 eV higher on the Rh_nCO^+ cluster than on Rh_n^+ . The kinetic data rather suggest that Rh_5CO^+ is a secondary reaction product resulting from the simple chemisorption of CO on the Rh_5^+ product.

C 2.2 CO chemisorption on $\text{Rh}_6\text{N}_2\text{O}^+$

Figure 6 shows the kinetic data for the $\text{Rh}_6\text{N}_2\text{O}^+$ reaction which shows some marked differences to the $n=5$ reaction. Rh_6O^+ is the single most intense product commensurate with k_2 (the N_2O decomposition reaction) exceeding k_0 (the reduction oxidation reaction), see Table 2. Calculations suggest that slightly less energy is deposited into the $n=6$ parent upon CO chemisorption (1.78 eV compared with 2.22 eV for $n=5$). However, the additional internal degrees of freedom of the larger cluster make it a more effective bath for the dissipation of additional energy. In addition, the probability of a CO + O encounter occurring is reduced on the larger cluster resulting in a lower efficiency for the CO burning reaction.

In a further difference to the $\text{Rh}_5\text{N}_2\text{O}^+$ case, is clear from Figure 6 that Rh_6CO^+ is a primary reaction product and hence that the simple displacement of N_2O by CO does occur on $n=6$.

Figures 6 a) and b) show a comparison of fits to the experimental data including two and one isomers of the parent ion, respectively. Whilst some slight non-linearity in the decay of the $\text{Rh}_6\text{N}_2\text{O}^+$ signal is observed, the overall quality of the fits is comparable in both cases. If two

isomers are employed Table 2 suggests that only one of them undergoes the displacement reaction, and displays concomitantly low rate constants for surface decomposition processes, whilst the other isomer instead undergoes rapid N_2O decomposition. Far-IRMPD spectra proved inconclusive in unambiguously identifying the structure of Ar-tagged $\text{Rh}_n\text{N}_2\text{O}^+$ complexes and the presence of multiple isomers could not be ruled out.²³

C 2.3 CO chemisorption on $Rh_nON_2O^+$

Figure 7 shows the experimental data for $Rh_nON_2O^+$ ($n = 5, 6$) exposed to 2.6×10^{-8} mbar ^{13}CO . The presence of co-adsorbed oxygen atoms in the $Rh_nON_2O^+$ systems introduces a range of new reaction possibilities and necessitates a revision of the mechanism to which the data is fit. In the following mechanism, the pseudo first-order rate constants k_i' reflect analogous steps to those of k_i in the previous mechanism:

Primary Reactions:

Secondary Reactions:

The results of the fits to this mechanism assuming single and two isomers of the parent ion are shown in Figure 7 and the pseudo first order rate constants extracted from the fit are presented in Table 3. The case for the inclusion of multiple isomers is clear in the marked deviation from linearity of the $Rh_6ON_2O^+$ signal decay, less so for $Rh_5ON_2O^+$.

The lower abundance of the $Rh_nON_2O^+$ species in the cluster beam, together with the additional reaction channels results in larger scatter in the experimental data. Nevertheless, the effects of the additional O atom are clear to discern. In both $Rh_nON_2O^+$ species, the simple dioxide, $Rh_nO_2^+$ is the dominant product, with Rh_nO^+ initially produced almost as rapidly. Both

products are indicative of N₂O decomposition, with Rh_{*n*}O⁺ signifying the subsequent oxidation and loss of CO₂.

One very obvious difference between the *n* = 5 and 6 clusters is the production in the former of the bare Rh₅⁺ cluster. We attribute this primarily to the CO oxidation reaction, Rh₅O⁺ + CO, with a possible smaller contribution from the displacement oxidation reaction on the parent. No such reaction is observed in the *n* = 6 case indicating perhaps that the barrier to CO oxidation is markedly lower on Rh₅O⁺ than Rh₆O⁺. To test this hypothesis, the oxide clusters were isolated and stored in the presence of high pressure ¹³CO. After 10 s the ratio of Rh_{*n*}⁺ to Rh_{*n*}O⁺ signals was determined to be a factor 7 higher for *n* = 5 than for *n* = 6 indicating that the relevant rate constants differ by a factor of *ca.* 8.

In both cases, the Rh_{*n*}OCO⁺ products are most satisfactorily fit as secondary products arising from CO addition to Rh_{*n*}O⁺ (the “induction period” for the *n* = 6 cluster is clear in Figure 7 at early times). This implies that, by contrast with the Rh₆N₂O⁺, the CO/N₂O displacement reaction is at most a minor channel in the reactivity of Rh₆ON₂O⁺. Despite the quality of the fits, however, there has to be some doubt over whether Rh₅OCO⁺ is a secondary product. The pseudo first order rate constant *k*₄' for the association step is uncomfortably large even considering the significant dipole moments of the oxide (calculated to be 3.8 D for the putative global minimum structure of Rh₅O⁺, 2.2 D for Rh₆O⁺) and the additional contribution made to the geometric cross-section of the bare cluster (for which collision rate has been calculated using ADO theory) by decorating species.

For completeness, Table 4 shows calculated thermodynamic data for CO chemisorption reactions on Rh_{*n*}O⁺, Rh_{*n*}N₂O⁺ and Rh_{*n*}ON₂O⁺. The values in Table 4 refer to putative global minimum structures and not to spin-conserving reactions. The only notable size-effect observed in the thermodynamics arises from the anomalously high N₂O binding energy to the oxide

cluster Rh_5O^+ , a cooperative binding effect which has been discussed previously in the context of the differing behaviour of $\text{Rh}_5\text{N}_2\text{O}^+$ and $\text{Rh}_5\text{ON}_2\text{O}^+$ under infrared heating.²⁴ The data in Table 4 merely serves to reinforce the point that it is relative reaction barriers (*i.e.*, kinetic factors) rather than the overall reaction thermodynamics which govern the course of these cluster surface reactions. Accordingly, comparison of the type of kinetic data on well-characterised systems reported here with calculated reaction profiles will lead to important insight into the catalytic properties of small transition metal clusters.

D. Summary and Conclusions

Collisional excitation of nitrous oxide–decorated rhodium clusters, $\text{Rh}_n\text{N}_2\text{O}^+$ ($n = 5, 6$) with Ar has been shown to result in similar fragmentation processes as previously observed for infrared excitation of the same species supporting the notion that the excitation is thermal in nature. Simple desorption loss of N_2O competes with nitrous oxide decomposition (and associated N_2 loss) with the branching ratio of the former increasing with collision energy in the region $E_{\text{cm}} = 0 - 80$ eV for all clusters studied. The presence of co-adsorbed oxygen atoms (in $\text{Rh}_n\text{ON}_2\text{O}^+$ ($n = 5, 6$)) is shown to significantly enhance the relative probability of the decomposition channel consistent with a change in the relative barrier heights for the two processes. This effect is most prominent in the case of $\text{Rh}_5\text{N}_2\text{O}^+ / \text{Rh}_5\text{ON}_2\text{O}^+$ where the relative probabilities of desorption and reaction channels are reversed. These observations are consistent with a cooperative binding effect whereby N_2O has a higher binding energy to the oxide cluster than to the naked cluster.

In other experiments, reactive collisions of ^{13}CO with $\text{Rh}_n\text{N}_2\text{O}^+$ and $\text{Rh}_n\text{ON}_2\text{O}^+$ ($n = 5, 6$) have revealed intriguing details of the combined N_2O reduction / CO oxidation reactions on rhodium clusters. Clear size effects are observed in the reaction kinetics of $\text{Rh}_5\text{N}_2\text{O}^+$ and $\text{Rh}_6\text{N}_2\text{O}^+$ with different dominant reaction products. In particular, in reactions involving the $n = 5$ cluster, satisfactory kinetic fits could only be achieved with a mechanism assuming the Rh_nCO^+ species is a secondary reaction product. Apparently the $\text{CO} / \text{N}_2\text{O}$ displacement reaction does not occur with any appreciable probability on this cluster.

In reactions of CO with $\text{Rh}_n\text{ON}_2\text{O}^+$ the further insight into the cluster surface CO oxidation reactions. CO burning is observed to be considerably faster on Rh_5O^+ than on Rh_6O^+ . As a result, the bare Rh_5^+ cluster is a significant product in the $\text{Rh}_5\text{ON}_2\text{O}^+ + \text{CO}$ reaction, but, under similar conditions, no Rh_6^+ product is observed in the reactions of the $\text{Rh}_6\text{ON}_2\text{O}^+$ cluster.

Detailed reaction profile calculations will be required to fully interpret the results of these studies. However, yet again, the study of catalytically (and environmentally) important reactions on small isolated clusters has provided new insights into the chemistry at play whilst also uncovering intriguing size– and structure effects.

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Figures:

(double column)

Figure 1. Mass spectrum of $\text{Rh}_n\text{O}_m(\text{N}_2\text{O})_x^+$ species produced in the region of $n = 5, 6$ under the experimental conditions employed here. The asterisks indicate the various parent ion species, $\text{Rh}_5\text{N}_2\text{O}^+$, $\text{Rh}_6\text{N}_2\text{O}^+$, $\text{Rh}_5\text{ON}_2\text{O}^+$ and $\text{Rh}_6\text{ON}_2\text{O}^+$ investigated in this study.

Figure 2. Decomposition of $\text{Rh}_5\text{N}_2\text{O}^+$ complexes induced by collision with argon atoms showing clear evidence of both N_2O desorption and N_2 loss. Clusters were left to undergo collisions with argon ($p = 2 \times 10^{-8}$ mbar) for 1s following resonant excitation for a) $t_{\text{exc}} = 1 \mu\text{s}$ (black, $E_{\text{cm}} \approx 0.2$ eV) and b) $t_{\text{exc}} = 500 \mu\text{s}$ (red, $E_{\text{cm}} \approx 30$ eV). The latter is shown offset for clarity.

Figure 3. Relative intensity of parent and different daughter ion signals as a function of centre of mass collision energy under Ar CID conditions (see text for details). The same fragmentation channels are observed for all parent ions studied and all show an increasing propensity for N_2O desorption as the collision energy increases. In agreement with earlier IRMPD studies, $\text{Rh}_5\text{N}_2\text{O}^+$ exhibits unusually inefficient N_2O decomposition ($-\text{N}_2$ channel).

(double column)

Figure 4. Evolution of the mass spectrum of mass-selected $\text{Rh}_5\text{N}_2\text{O}^+$ and $\text{Rh}_6\text{N}_2\text{O}^+$ clusters exposed to 2.6×10^{-8} mbar ^{13}CO for 10 s.

Figure 5. Experimental data (symbols) and pseudo first order kinetic fits (shown as lines) for the reactions of $\text{Rh}_5\text{N}_2\text{O}^+$ with 2.6×10^{-8} mbar ^{13}CO . Rh_5CO^+ is fit as a secondary product whereas Rh_5^+ and Rh_5O^+ are primary products (see text for details).

Figure 6. Experimental data (symbols) and kinetic fits (lines) for the reactions of $\text{Rh}_6\text{N}_2\text{O}^+$ in 2.6×10^{-8} mbar ^{13}CO . The fit shown in b) assumes the presence of two isomers of $\text{Rh}_6\text{N}_2\text{O}^+$, that in a), just one. All products are fit as primary reaction products.

(double column)

Figure 7. Experimental data (symbols) and kinetic fits to the mechanism in the text (lines) for the reactions of $\text{Rh}_n\text{ON}_2\text{O}^+$ exposed to 2.6×10^{-8} mbar ^{13}CO (see text for details). The fits in the upper graphs assume a single isomer of the parent ion, the lower graphs two.

Tables

Table 1. Calculated CO binding energies to various Rh_5^+ and Rh_6^+ – based species are presented for a range of spin states. Values in bold indicate calculated binding energies to the lowest energy calculated structures (shown). Red, black, blue and green are used to present O, C, N and Rh atoms, respectively.

Calculated CO binding energy /eV				
$n=$	$2S+1=$	Rh_nCO^+	Rh_nOCO^+	$\text{Rh}_n\text{N}_2\text{OCO}^+$
5	5	-1.89	-2.17	-2.11 ²
	7	-2.22	-2.29	-2.27
	9	-1.67	-2.06	-1.75

6	8	-1.78	-2.32	-1.89
	10	-1.78 ¹	-2.04	-1.72 ²
	12	-1.71	-1.79	-1.70 ²

¹Differs from the structure shown in that CO is atop-bound

² CO bound in different hollow site to that in the structure shown

Table 2. Pseudo first-order rate constants for the reactions of $\text{Rh}_n\text{N}_2\text{O}^+$ ($n = 5, 6$) in 2.6×10^{-8} mbar ^{13}CO (see text for details of the mechanism and Figures 5, 6 for fits).

	$\text{Rh}_5\text{N}_2\text{O}^+$		$\text{Rh}_6\text{N}_2\text{O}^+$		
	2 isomer fit $/\text{s}^{-1}$		1 isomer fit $/\text{s}^{-1}$	2 isomer fit $/\text{s}^{-1}$	
	A	B		A	B
%	61	39	100	69	31
k_0	0.40	1.80	0.33	0.11	1.13
k_1	0.00	0.00	0.19	0.26	0.00
k_2	0.17	0.23	0.46	0.41	0.72
k_3	0.03		0.01	0.02	
k_4	0.06		0.03	0.00	

Table 3. Pseudo first-order rate constants for the reactions of $\text{Rh}_n\text{ON}_2\text{O}^+$ in low-pressure ^{13}CO atmosphere (see text for details of the mechanism and Figure 7 for fits).

	$\text{Rh}_5\text{ON}_2\text{O}^+$			$\text{Rh}_6\text{ON}_2\text{O}^+$		
	1 isomer fit $/\text{s}^{-1}$	2 isomer fit $/\text{s}^{-1}$		1 isomer fit $/\text{s}^{-1}$	2 isomer fit $/\text{s}^{-1}$	
		A	B		A	B
%	100	75	25	100	76	24
k_0'	0.23	0.34	0.00	0.38	0.64	0.07
k_1'	0.00	0.00	0.00	0.00	0.00	0.00
k_2'	0.33	0.06	2.14	0.41	0.67	0.05
k_3	0.11	0.23		-	0.00	
k_3'	0.10	0.00		0.02	0.00	
k_4'	1.48	1.44		0.26	0.24	
k_5'	0.08	0.03	0.00	-	-	
k_6'	0.00	0.00		-	-	

Table 4. Calculated thermodynamic data for cluster reactions induced by chemisorption of CO. *n.b.*, all data refer to putative global minimum structures and not necessarily to spin conserving reactions.

Reaction	ΔE / eV	
	$n=5$	$n=6$
$\text{Rh}_n\text{O}^+ + \text{CO} \rightarrow \text{Rh}_n^+ + \text{CO}_2$	-1.66	-1.81
$\text{Rh}_n\text{N}_2\text{O}^+ + \text{CO} \rightarrow \text{Rh}_n^+ + \text{CO}_2 + \text{N}_2$	-2.88	-2.85
$\text{Rh}_n\text{N}_2\text{O}^+ + \text{CO} \rightarrow \text{Rh}_n\text{O}^+ + \text{CO} + \text{N}_2$	-1.21	-1.04
$\text{Rh}_n\text{ON}_2\text{O}^+ + \text{CO} \rightarrow \text{Rh}_n^+ + \text{CO}_2 + \text{N}_2\text{O}$	-0.52	-1.02
$\text{Rh}_n\text{ON}_2\text{O}^+ + \text{CO} \rightarrow \text{Rh}_n\text{O}^+ + \text{CO}_2 + \text{N}_2$	-2.45	-2.80
$\text{Rh}_n\text{ON}_2\text{O}^+ + \text{CO} \rightarrow \text{Rh}_n\text{O}_2^+ + \text{CO} + \text{N}_2$	-1.23	-1.40