

# Dramatic size effects and evidence of structural isomers in the reactions of rhodium clusters, $\text{Rh}_n^{+/-}$ , with nitrous oxide

Daniel Harding,<sup>a</sup> Mark S. Ford,<sup>a</sup> Tiffany R. Walsh<sup>a,b</sup> and Stuart R. Mackenzie,<sup>a,\*</sup>

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The reactions of gas phase rhodium clusters,  $\text{Rh}_n^{+/-}$  ( $n < 30$ ), with nitrous oxide,  $\text{N}_2\text{O}$ , have been investigated under single collision conditions by Fourier transform ion cyclotron resonance mass spectrometry. The only significant reaction observed is the sequential generation of oxides. Absolute rate constants for the reactions of all clusters have been determined and, in the case of the cationic clusters especially, exhibit large fluctuations as a function of cluster size with local minima observed for  $n = 5, 19, 28$ . Striking similarities are observed with the variation in rate constants for these clusters in reactions with small hydrocarbons [C. Aldhart and E. Uggerud, *J. Chem. Phys.*, 2005, **123**, 214709]. Corresponding size effects are also observed but are less marked in the reactions of the anionic clusters. The reactions of several clusters exhibit marked deviations from simple pseudo-first order kinetics suggesting the presence of multiple isomeric forms:  $\text{Rh}_{11}^+$ ,  $\text{Rh}_{12}^+$  and  $\text{Rh}_8^-$  exhibit characteristic bi-exponential decays which are interpreted in terms of the existence of different structural forms of the cluster which have markedly different reactivity. By contrast,  $\text{Rh}_6^+$ ,  $\text{Rh}_7^+$  and  $\text{Rh}_8^+$  show rates which apparently increase with time, probably due to collisional activation. Thermalisation of the clusters prior to reaction by exposure to pulses of argon results in changes to the kinetics of these anomalous systems which can be explained in terms of collision induced isomerisation.

## I. Introduction

Much of the research into the reactions of small transition metal clusters has been motivated by the idea that they represent tractable model systems for the highly dispersed catalysts found in many industrial processes. It has been argued that clusters, with no long range order, represent a high concentration of the defect sites which so often provide the active sites for interesting chemistry to occur on extended surfaces. Consequently there is considerable interest in the study of the relationship between the structure and reactivity of clusters.<sup>[1]</sup>

Quite apart from any practical application, it has become clear that small transition metal clusters exhibit many fascinating and unique properties.<sup>[2,3]</sup> In particular, studies of the reaction kinetics of metal clusters with small molecules have demonstrated dramatic cluster size dependence of reaction rate constants.<sup>[2-10]</sup> More recently, it has become clear that as well as the *number* of atoms, in some systems the geometrical structure of the cluster also plays an important role in reactivity. In experiments, such effects are usually revealed as biexponential kinetic plots for the reactions of particular clusters. These have been explained in terms of the co-existence of multiple isomers of the cluster which have significantly different reactivities.<sup>[11-18]</sup> Supporting evidence for such an interpretation has subsequently come from

photoionization<sup>[19]</sup>, far infra-red multiphoton dissociation studies, which have resolved different isomers in particular clusters,<sup>[20]</sup> and from computational studies of structural isomerism.<sup>[21,22]</sup>

In this study we have used Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry to investigate the reactivity of small rhodium clusters,  $\text{Rh}_n^{+/-}$  ( $n = 5-30$ ) towards nitrous oxide,  $\text{N}_2\text{O}$ . This reaction has practical implications in terms of the use of rhodium as the reduction catalyst in the automobile three-way catalytic converter.<sup>[23]</sup> The naturally monoisotopic nature of rhodium has long made it a favourite for experimental study using mass spectrometric techniques and  $\text{Rh}_n^{+/-}$  reactions with  $\text{CO}$ ,<sup>[10]</sup>  $\text{NO}$ ,<sup>[14,24]</sup> benzene,<sup>[25]</sup> azidoacetonitrile,<sup>[26]</sup> and small alkanes<sup>[27-29]</sup> have been studied previously. In reactions with  $\text{CO}$ ,  $\text{NO}$  and benzene, reaction rates generally increase monotonically with cluster size in line with the rates predicted by collision theories.<sup>[30]</sup> Biexponential kinetics have been observed in relatively few systems ( $\text{Rh}_6^+$  and  $\text{Rh}_5^+$  with  $\text{NO}$ ,<sup>[14]</sup> and  $\text{Rh}_{12}^+$  with ethane and isobutane<sup>[28]</sup>) perhaps reflecting the often very high reactivity of rhodium clusters which is probably dominated by electronic effects. Even in systems exhibiting smooth size dependence, however, the *mechanism* of reaction often changes significantly with cluster size and structure. This is particularly true of the branching ratios for the various dehydrogenation products observed in the reactions of  $\text{Rh}_n^+$  with benzene and of the decomposition of nitric oxide on rhodium clusters. In the latter case, some clusters react very differently to adjacent cluster sizes (i.e., clusters differing by just one atom), despite having similar sticking probabilities.<sup>[24]</sup>  $\text{Rh}_{13}^+$ , for example, simply adsorbs multiple nitric oxide molecules without evolving  $\text{N}_2$  whilst all other

<sup>a</sup> Department of Chemistry, University of Warwick, Coventry. CV4 7AL

<sup>b</sup> Centre for Scientific Computing, University of Warwick, Coventry. CV4 7AL

\*Corresponding author, current address: University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW.

Email srm49@cam.ac.uk

small clusters ( $n < 17$ ) are very efficient in decomposing multiple NO molecules, generating high oxide clusters.<sup>[24]</sup>

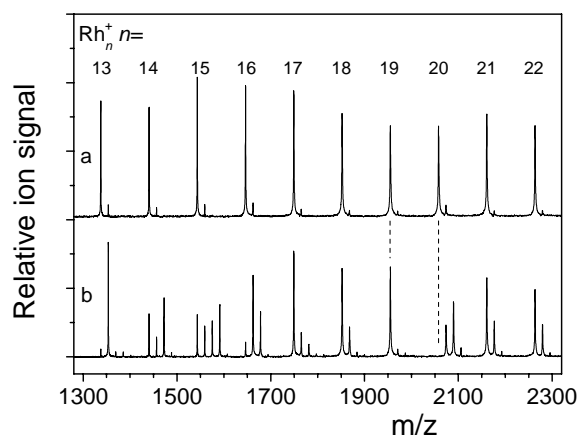
Reactions of various nitrogen oxides with clusters of other metals have been studied due to the practical importance of these reactions in catalysis. Of particular relevance to the present study, platinum clusters react rapidly with N<sub>2</sub>O releasing gaseous N<sub>2</sub>,<sup>[31]</sup> the rate of reaction depending strongly on the cluster size with rather similar trends observed for cations and anions. Similarly, the reactions of N<sub>2</sub>O on extended rhodium surfaces have been studied<sup>[32–35]</sup> and show that dissociation yielding gaseous N<sub>2</sub> and adsorbed O atoms occurs on polycrystalline rhodium surfaces over a wide range of temperatures.<sup>[35]</sup> Several studies have demonstrated that different single crystal surfaces show considerable variation in their reaction with N<sub>2</sub>O.<sup>[33,34]</sup> N<sub>2</sub>O exhibits a sticking probability of 0.5 on Rh(110) at room temperature and decomposes to molecular nitrogen and O atoms with the former desorbing. By contrast the Rh(111) surface is quite unreactive towards N<sub>2</sub>O even up to 900K.

We have studied the reactions of N<sub>2</sub>O with both cationic and anionic rhodium clusters, Rh<sub>*n*</sub><sup>+/-</sup> ( $n < 30$ ) by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry and present here the cluster size-dependent rate constants and strong evidence for the co-existence of multiple isomeric forms of several clusters.

## II. Experimental

All experiments were performed using a 3T FT-ICR mass spectrometer (Bruker Daltonics Apex II) fitted with an external laser ablation cluster source developed from an original design by Berg *et al.*<sup>[36]</sup> Our version has been described in detail elsewhere<sup>[14,24,36]</sup> but briefly, a frequency doubled Nd:YAG laser pulse (*ca.* 3 mJ, 532 nm, 8 ns) is focused onto a rotating rhodium foil target (Aldrich). The resulting plasma is entrained in a pulse of helium from a homemade piezo valve with a backing pressure of 15–30 bar and travels down a 30 mm long, 2 mm diameter clustering channel before expansion into the source chamber, maintained at  $\sim 10^{-7}$  mbar ( $10^{-4}$  mbar during He gas pulsing). The beam is then skimmed and cluster ions guided through differentially pumped stages into a 60 mm diameter cylindrical infinity cell maintained at a base pressure of *ca.*  $2 \times 10^{-10}$  mbar. Storing anionic / cationic clusters is a simple matter of reversing the polarity of the ion optics. To increase the signal to noise ratio, ions are typically accumulated for 16 laser pulses. The kinetic energy of the rhodium cluster ions is limited by a 1.5 V axial trapping potential, giving a maximum centre of mass collision energy for collisions with N<sub>2</sub>O of *ca.* 160 meV for  $n = 4$  and 22 meV for  $n = 29$ .

Reactions were performed by controllably leaking N<sub>2</sub>O (99.5%, Argo) into the ICR cell ( $8 \times 10^{-10}$  mbar  $< P < 5 \times 10^{-8}$  mbar) with mass spectra of the ICR cell contents recorded as a function of time. The cell pressure was calibrated according to the method described previously,<sup>[24]</sup> permitting *absolute* rate constants to be determined with an estimated uncertainty of  $\pm 50\%$  (although the variation in rate between different



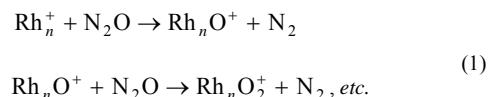
**Fig. 1** Time evolution of the mass spectrum of Rh<sub>*n*</sub><sup>+</sup> clusters exposed to  $1 \times 10^{-8}$  mbar N<sub>2</sub>O. The upper spectrum represents time  $t = 0$  and the lower  $t = 20$ s exposure. The variation in the reactivity with cluster size is highlighted for adjacent clusters  $n = 19, 20$ : Rh<sub>19</sub><sup>+</sup> is essentially unreactive whilst under identical conditions the naked Rh<sub>20</sub><sup>+</sup> cluster has completely reacted.

clusters is considerably better determined).<sup>[30]</sup> In order to determine the relative reaction rates of adjacent clusters as accurately as possible, the reactions of all cluster sizes were performed simultaneously. Additional isolation studies were performed on each cluster size to confirm that no fragmentation of any cluster takes place. In performing these studies it was found that in the reactions of the very smallest anionic clusters, Rh<sub>*n*</sub><sup>-</sup> ( $n < 6$ ), the integrated cluster signal falls significantly with time. No smaller clusters were observed and we attribute this observation to charge transfer reactions. As a result it is impossible to determine the reactivity towards N<sub>2</sub>O and the reactions of these clusters are not discussed below. For some experiments, notably the reactions of clusters which exhibit anomalous reaction kinetics, we attempted to “thermalise” the clusters to room temperature prior to reaction by admitting pulses of argon directly to the cell through a pulsed valve.

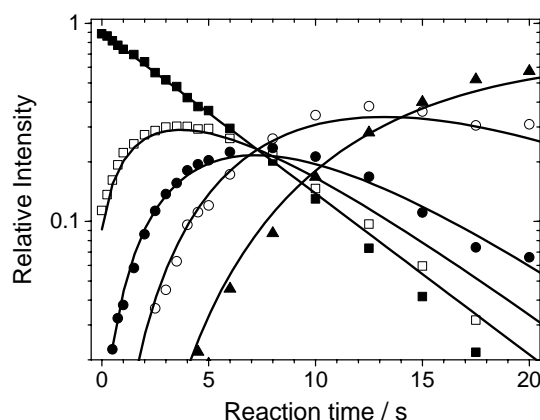
## III. Results and Discussion

### A. Cluster Size-Effects

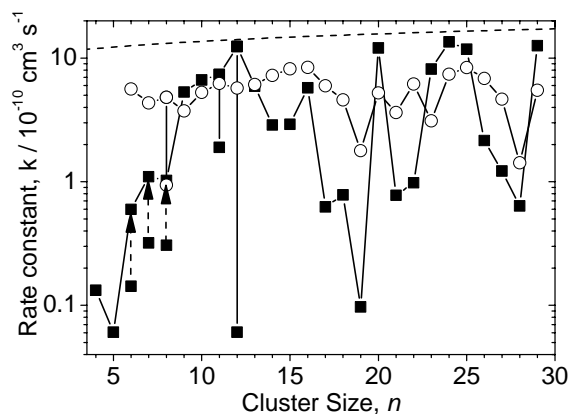
Figure 1 shows the time evolution ( $t = 0$  and 20 s) of the mass spectrum of a range of Rh<sub>*n*</sub><sup>+</sup> clusters during exposure to  $1 \times 10^{-8}$  mbar N<sub>2</sub>O. For all clusters studied the overwhelmingly dominant reaction observed is the sequential addition of oxide atoms:



If any intermediate [Rh<sub>*n*</sub>N<sub>2</sub>O]<sup>+/-</sup> adduct is involved, its lifetime is too short for it to be observed on the timescale of the FT-ICR experiment. It is already clear from the data in



**Fig. 2** Semi-logarithmic plot of reaction kinetics for  $\text{Rh}_7^-$  cluster reactions with  $\text{N}_2\text{O}$ . The data represents the relative fractions of  $\text{Rh}_7^-$  (filled squares),  $\text{Rh}_7\text{O}^-$  (open squares),  $\text{Rh}_7\text{O}_2^-$  (filled circles),  $\text{Rh}_7\text{O}_3^-$  (open circles) and  $\text{Rh}_7\text{O}_4^-$  (filled triangles). Larger products are omitted for clarity but included in the fits.



**Fig. 3** The bimolecular rate constants for the reactions of rhodium cluster anions (open circles) and cations (closed boxes) with  $\text{N}_2\text{O}$  illustrating the size-dependence of the reactivity. In the case of cationic clusters  $n = 6-8, 11, 12$  and the  $n = 8$  anionic cluster the kinetics are more complex and cannot be described by a single rate constant. In these cases either two rates are shown above or a range of rates indicated. The anomalous kinetics of these clusters are illustrated in Figure 4.

Figure 1 that there is substantial variation in the reactivity of the bare clusters towards  $\text{N}_2\text{O}$ . For example, after 20 s at this pressure, no naked  $\text{Rh}_{20}^+$  clusters remain, all having reacted to produce  $[\text{Rh}_{20}\text{O}_m]^+$ ,  $m = 1, 2, 3$ . By contrast, the  $\text{Rh}_{19}^+$  cluster shows barely any sign of having reacted at all under identical conditions, with no products observed. The variation does not end with the first reaction step. It is also clear from Figure 1 that the naked  $\text{Rh}_{13}^+$  reacts quickly in the first step to generate  $[\text{Rh}_{13}\text{O}]^+$  but that the oxide cluster, in turn, is comparatively unreactive. This is not the case for other clusters, such as  $\text{Rh}_{15}^+$  in which the first step is not as rapid as for  $n = 13$  but which proceeds to generate multiple oxide products. A detailed study of the reactivity of the oxide clusters is under way in our laboratory but for the present article we restrict ourselves to discussion of the first reaction step.

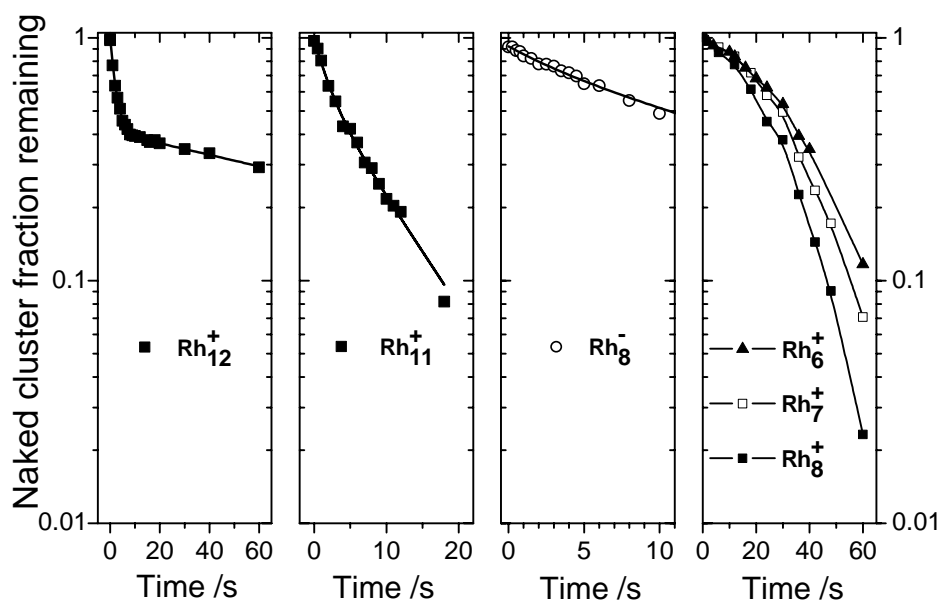
By assuming pseudo-first order kinetics for each reactive step it is possible to fit the kinetics and extract rate constants for each reaction step. By way of illustration, such a kinetic fit is shown in Figure 2 for the  $\text{Rh}_7^- + \text{N}_2\text{O}$  reaction. In common with the vast majority of cluster sizes, the first step ( $\text{Rh}_7^- + \text{N}_2\text{O} \rightarrow \text{Rh}_7\text{O}^-$ ) exhibits clear pseudo-first order kinetics. The handful of anomalous clusters in which this is not the case are considered separately below.

From the pseudo-first order kinetic plots, it is possible, with knowledge of the reactant gas pressure, to determine the absolute rate constants for the reaction of each cluster. These are summarized in Figure 3 from which several striking observations can be made. One of the key findings of this study is the manner in which the reactivity of the cationic clusters fluctuates as a function of cluster size. In the size range studied here, the reaction rate constant varies by almost three orders of magnitude. In fact in some cases (*e.g.*,  $n = 19, 20$ ) differences of two orders of magnitude are observed between adjacent cluster sizes. In this, the trend in reactivity versus cluster size has more in common with the reactions of  $\text{Rh}_n^+$  with small hydrocarbons<sup>[28]</sup> than with diatomic molecules, benzene and azidoacetonitrile. Indeed some similarities with the hydrocarbons are marked: The relative unreactivity of the  $n = 5, 17-19$  and 28 cationic clusters is a

feature common to the reactions with ethane, propane and isobutane, as is the local maximum in reactivity for cluster sizes  $n = 16, 20$ .

Although far from monotonic, the variations in reaction rate versus cluster are noticeably less pronounced for the anionic clusters than for the cations. As mentioned above, rate constants could not be determined for the very smallest anions ( $n < 6$ ) as these clusters appear to react by either charge transfer or collision/reaction induced electron detachment rendering them neutral (and thus undetectable). Despite the less marked size-dependence of reactivity of the  $\text{Rh}_n^-$  clusters, it is notable that the minima in reactivity for  $n = 19, 28$  are reproduced. The wide variation in reaction rate for cationic clusters and a much smoother variation for anionic clusters is similar to that seen for the reactions of Pt clusters with  $\text{N}_2\text{O}$ .<sup>[31]</sup> In many other systems, however, the sign of the charge on the cluster has been observed to make little difference to the reaction rate. The fact that this is not the case here may be related to the fact that vertical electron attachment to  $\text{N}_2\text{O}$  is dissociative.<sup>[37]</sup> If electron transfer can occur between the small clusters and an  $\text{N}_2\text{O}$  molecule that is on or close to the surface of the cluster, dissociation of the  $\text{N}_2\text{O}$  molecule is guaranteed. This would have the effect of increasing the reaction efficiency independently of any geometrical structural effects and would account for the fact that at small  $n$  the anionic clusters are considerably more reactive than the cations. The larger anions, however, with their correspondingly higher electron affinities react more similarly to the cationic clusters. Even with larger clusters the presence of the negative charge may lower the barrier to dissociation of  $\text{N}_2\text{O}$  at the cluster surface, mitigating the structural effects which cause the dips in reactivity for the cationic clusters.

It is informative to compare the measured rate constants with those calculated by various collision theories. Figure 3 also shows the calculated collision rates assuming the surface charge capture (SCC) model of Kummerlöwe and Beyer.<sup>[30]</sup>



**Fig. 4** Unusual reaction kinetics exhibited by a sub-set of clusters: Biexponential kinetics of  $\text{Rh}_{12}^+$ ,  $\text{Rh}_{11}^+$  and  $\text{Rh}_8^-$ , and rates which appear to increase with time,  $\text{Rh}_n^+$  ( $n = 6-8$ ).

This model, an adaptation of the average dipole orientation (ADO) model<sup>[38]</sup>, treats the cluster as a perfectly conducting sphere and permits the charge to migrate to the surface of the cluster. In reactions of  $\text{Rh}_n^{+/-}$  with nitric oxide<sup>[24]</sup> the SCC model was found to reproduce well both the absolute magnitude of the rate constants and the relatively smooth trend in reactivity with  $n$ . In this case, however, few clusters react at rates approaching the SCC collision limit with most demonstrating reaction efficiencies of 1-50%. Again this is similar to the reaction efficiencies found for reactions with small alkanes (though in this case comparison was made with rates calculated for reactions of point charges).<sup>[28]</sup> It is tempting to propose that the larger variations in reaction rate observed for these less efficient reactions results from the increased importance of the geometrical structure in determining the reactivity. In the present case, the main factor determining the reaction probability is the likelihood of  $\text{N}_2\text{O}$  dissociation at the surface of the cluster. It would be surprising if this efficiency were not strongly affected by the size and shape of the cluster. In general, larger clusters can dissipate energy more efficiently due to their larger number of vibrational degrees of freedom. This results in more sticky collisions (*i.e.*, longer residence times) compared with smaller clusters. Such reasoning could account for the low reaction rates seen for cations with  $n < 8$ . The observation of the oxide clusters as the only products in the first step implies there is at most a small barrier to dissociation once an  $\text{N}_2\text{O}$  molecule is adsorbed on the cluster surface.

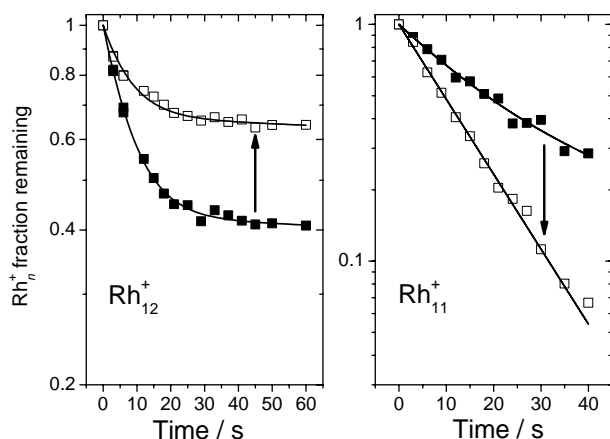
Another reason for the relative unreactivity of the smaller clusters may lie in the mechanism of the reaction itself. The  $\text{N}_2\text{O}$  molecule is longer than the largest dimension of the smallest clusters studied here. Preliminary calculations of the likely mechanism indicate that a key step in the dissociation pathway involves the molecule bending to bind with the cluster at both N- and O- ends of the molecule. Clearly this will not be possible on the smallest clusters without extreme bending of the adsorbate molecule.

## B. Evidence for multiple isomers

In examining the kinetics of a small number of cluster sizes it proved impossible to fit the first step kinetics as a pseudo-first order process. In these cases ( $\text{Rh}_n^+$ ,  $n = 6 - 8$ , 11, 12 and  $\text{Rh}_8^-$ ) either two different rates are indicated on Figure 3 or else a range of rates are marked. The non linearity of the first order plots fall into two distinct categories which we treat separately.

### (i) $\text{Rh}_{11}^+$ , $\text{Rh}_{12}^+$ & $\text{Rh}_8^-$ : Biexponential reaction kinetics

Figure 4 shows pseudo first order kinetic plots for the  $\text{Rh}_{11}^+$ ,  $\text{Rh}_{12}^+$  and  $\text{Rh}_8^-$  clusters. In each case, the plots show marked deviation from linearity and, as the fits demonstrate, can be better modeled as a sum of two exponential decays.<sup>[11-18]</sup> The rationale behind such a fit is that i) there exist within our sample at least two different forms of each of these clusters with significant abundance (more than a few per cent of the total) and ii) that these forms have markedly different reactivities towards  $\text{N}_2\text{O}$ , *i.e.*, one component much more reactive than the other. Clearly, even better fits could be obtained assuming polyexponential decays but there is no justification in the data for this. The fact that most clusters do not exhibit such kinetics and are well modeled by single exponential decays does not, of course, prove that only one form exists; The reactivity of both forms may be very similar or else the relative proportion of one very small.  $\text{Rh}_{12}^+$  has previously been found to exhibit fast and a slow reacting components in reactions with small alkanes.<sup>[28]</sup> It is possible that the different forms of the clusters are different spin states of the clusters. Our recent DFT calculations on the neutral and cationic  $\text{Rh}_6$  clusters identified low-lying isomers of many different spin multiplicities.<sup>[22]</sup> However, spin-orbit coupling will inevitably perturb these states and, given the long timescales involved in the experiments (several seconds), it is likely that the most stable electronic state (within the 3T



**Fig. 5** The effect of thermalisation by collisions with argon gas pulses on the kinetics of the  $\text{Rh}_{12}^+$ ,  $\text{Rh}_{11}^+$  clusters. The kinetics of the nascent cluster distribution are shown by filled squares, those following thermalisation with argon pulses are shown with open squares. In the case of  $\text{Rh}_{12}^+$ , collisions result in an increase in the fraction of the relatively unreactive component. The reverse is true for  $\text{Rh}_{11}^+$ .

thermalisation kinetics to a simple sum of two exponential decays:

$$\frac{[\text{Rh}_n^+](t)}{[\text{Rh}_n^+]_0} = A \exp(-k_{\text{fast}}^* t) + (1 - A) \exp(-k_{\text{slow}}^* t), \quad (2)$$

where  $k_{\text{fast}}^*$ , and  $k_{\text{slow}}^*$  are the pseudo first order rate constants for the fast and slow reacting components, respectively and  $A$  is the fractional composition of the more reactive component. The results of the fits to the experimental data are shown in Table 1.

**Table 1.** Fit of the  $\text{Rh}_{11}^+$  and  $\text{Rh}_{12}^+$  kinetic data in Figure 5 to a sum of two exponential decays. The uncertainties given indicate the quality of the fits rather than absolute uncertainties.

	$\text{Rh}_{11}^+$		$\text{Rh}_{12}^+$	
	Original	Thermalised	Original	Thermalised <sup>a</sup>
$k_{\text{fast}}^*$	0.073(1)	0.073(1)	0.1230(5)	0.1230(5)
$k_{\text{slow}}^*$	0.019(4)	--	0.0006(6)	0.0006(6)
$A$	0.45	1.0	0.58	0.34
$R^2$		0.9954	0.9989	0.9896

<sup>a</sup> rate constants fixed at their non-thermalised values, only  $A$  fitted

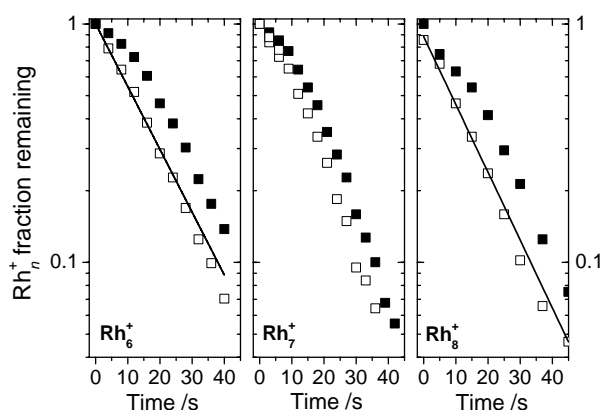
magnetic field) is reached. A more likely explanation, and the one more commonly invoked to account for this type of kinetics, is that the different forms are structural isomers of the same cluster. By definition these will have different geometrical forms and, it seems reasonable to assume, different reactivities. Our calculations have indeed identified two low-lying structures of  $\text{Rh}_6^+$  that support markedly different barriers to reaction with NO and thus can plausibly account for the biexponential kinetics of this cluster.<sup>[14]</sup>

One way in which we might expect different isomers to be present in our ion distribution is if, during the supersonic expansion, a fraction of the clusters remained trapped behind a local barrier which prevented them from adopting the global minimum structure. Such phenomena are common in molecular beam work, especially with strong expansions such as those used here, and often lead to non-Boltzmann populations in different internal energy modes.<sup>[39]</sup> In order to test this hypothesis, experiments were undertaken to thermalise the clusters trapped within the ICR cell prior to reaction. This was achieved by subjecting the ions to pulses of argon immediately following their trapping in the cell. Multiple collisions with this background gas should perturb the internal energy of the cluster distribution resulting in a sample better characterized as room temperature. With a simple model of the argon gas pulse as measured using a fast ion gauge, and based on calculated collisional cross-sections we estimate that during a single 1000 ms gas pulse (which raises the ICR cell pressure momentarily to *ca.*  $10^{-6}$  mbar) a typical cluster will undergo approximately 20 collisions with argon atoms each at near thermal centre of mass collision energy. This pulse of gas is typically pumped away in  $<1$  s leaving only the background reactant gas. Following the argon pulse, reactions were performed exactly as before. The result of thermalisation on the reaction kinetics is shown in Figure 5. In an attempt to quantify the effects of thermalisation and in line with our Occam's razor approach to understanding the underlying chemistry, we have fit the original and post-

Intriguingly, the effect of thermalisation on the reaction kinetics is qualitatively different for the  $\text{Rh}_{11}^+$  and  $\text{Rh}_{12}^+$  clusters. In the case of the former, the data prior to thermalisation is best fit by two rate constants differing by a factor of  $3.8 \pm 0.8$  with the more reactive component representing *ca.* 45% of the total. Multiple collisions with argon eliminate the characteristic biexponential decay leading to simple pseudo-first order kinetics. The rate constant derived from the new plot is consistent with the faster of the two rates deduced from the original biexponential decay. Our interpretation, therefore, is that thermalisation has the effect of converting all  $\text{Rh}_{11}^+$  clusters into the more reactive structural form. The two sets of kinetic data for  $\text{Rh}_{11}^+$  were fit simultaneously with the rate constant for the reactive component of the nascent cluster distribution fixed to be the same as the rate constant as derived from the thermalised data.

By contrast, even following thermalisation the kinetics of the  $\text{Rh}_{12}^+$  cluster remain distinctly bi-exponential. Fitting the non-thermalised data yields rate constants in this case differing by a factor of  $>200$ . In Table 1 we have fit the kinetic data following thermalisation using the same reactive rate constants as the original and fit only the relative fraction of each component. It is clear from both Figure 5 and Table 1 that this gives a good fit. In other words, within the two isomer interpretation, the effect of the argon pulse in this case is to increase significantly the relative fraction of the more unreactive component.

If our interpretation of these observations is correct, the  $n = 11$  and  $12$  cationic clusters have at least two low-lying isomeric structures which may be interconverted by means of thermal collisions. It remains a challenge to theory to determine if this is the case. DFT calculations on transition metal clusters of this size are computationally demanding, but



**Fig. 6** The effect of argon gas pulses on the kinetics of the  $\text{Rh}_n^+$  ( $n = 6 - 8$ ) clusters with  $\text{N}_2\text{O}$ . The kinetics of the nascent cluster distribution is shown by closed squares, those following thermalisation with argon pulses are shown with open squares. The lines on the  $n = 6, 8$  data represent fits assuming simple pseudo first order kinetics.

one of us has recently published a detailed computational study of structural isomerism in the  $\text{Nb}_{10}^+$  cluster.<sup>[21]</sup>

#### (ii) $\text{Rh}_n^+$ , $n=6-8$ : accelerating rates

The  $n = 6, 7, 8$  cationic clusters exhibit qualitatively different kinetic behaviour as shown in the right hand panel of Figure 4. The slope of the first order kinetic plot, i.e., the rate of reaction, in these cases apparently increases with time. The interpretation of these observations is more challenging than case (i) above but again such effects have been seen in other systems. Most notably, such an accelerating rate was observed in the reaction of the rhodium monomer cation,  $\text{Rh}^+$ , with benzene<sup>[40]</sup>. In this case the behaviour was attributed to collisional deactivation of an electronically excited state generating a more reactive ground state. In their study of rhodium cluster reactions with hydrocarbons, Aldhart and Uggerud comment that they deliberately thermalised their clusters prior to reaction of avoid contributions from long lived-states. Clearly in the case of the monomer cation,  $\text{Rh}^+$ , electronic energy is the only internal degree of freedom and thus either it or translational energy must be responsible. In the case of clusters, however, the effects of unreactive collisions upon several internal energy modes must be considered. In addition to perturbing the translational energy distribution (and thus the centre of mass collision energy), unreactive collisions can cause vibrational heating / cooling as well as potentially inducing isomerization as implicated above. It is clear from Figure 3 that in the case of these small cationic clusters the majority of collisions with  $\text{N}_2\text{O}$  are unreactive (the reaction rate being more than an order of magnitude lower than the calculated collision rate) and thus the average cluster undergoes several unreactive collisions prior to reacting. If the effect of an unreactive collision was to generate a more reactive form of the cluster – for example, an excited electronic or vibrational level, or a more reactive isomeric form – then the overall rate would indeed appear to accelerate with increasing time as seen in Figure 4.

Interestingly, in reactions with nitric oxide, the  $\text{Rh}_6^+$  cluster exhibits biexponential kinetics implying the presence of multiple isomers. We cannot discount the possibility that the increased rate arises due to the effects of collision on the translational energy distribution of our clusters, but the fact that  $\text{Rh}_5^+$  and  $\text{Rh}_9^+$  clusters show simple pseudo-first order behaviour is difficult to explain in this case.

Figure 6 illustrates the effects of thermalisation on the kinetics of the  $\text{Rh}_n^+$  ( $n = 6 - 8$ ) clusters. Post-thermalisation,  $\text{Rh}_6^+$  and  $\text{Rh}_8^+$  clusters exhibit simple pseudo first order kinetics with rates consistent with those at longer reaction times without the argon pulse. The  $\text{Rh}_7^+$  kinetic plot still exhibits some slight non-linearity post thermalisation which decreases further with multiple argon pulses indicating that a single argon pulse is perhaps insufficient for complete thermalisation. Thus, for these clusters it is clear that collisional activation is important and given the observation of multiple isomers of  $\text{Rh}_6^+$  in identical experiments with NO, collisional-induced isomerisation again seems the most plausible explanation.

## IV. Summary and Conclusions

The reactions of small charged rhodium clusters with nitrous oxide have been investigated by FT-ICR mass spectrometric techniques. The principal reaction observed is the sequential addition of oxygen atoms to the naked clusters the rate of which provide a sensitive probe of the electronic and geometrical structure of the cluster. The rates of reaction observed are generally significantly below the collision rate as calculated using the surface charge capture model. Large variations in the rates of reactivity with cluster size are observed for the reactions of the cationic clusters. The local maxima and minima observed show striking similarity to the similar features observed in reactions with small alkanes. The anionic clusters exhibit smaller fluctuations and the very smallest ( $n < 6$ ) appear to undergo additional decay processes by some charge transfer mechanism.

The reaction kinetics of several clusters suggest the presence of multiple isomers in our experiments. To test this interpretation the clusters have been subjected to thermalising pulses of argon prior to reaction. The results of these experiments can be understood in terms of collision-induced isomerization and collision-induced activation.

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