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Size-dependent dehydrogenation of ethane by cationic rhodium clusters in the gas phase

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Dedicated to Prof. Diethard K. Bohme on the occasion of his 65th birthday.

Abstract

The reactivity of cationic rhodium clusters, Rh_n^+, $n = 1–23$, with ethane is studied by Fourier transform ion cyclotron resonance mass spectrometry. Single and double dehydrogenation with elimination of molecular hydrogen are the reactions observed. The reaction efficiency and branching ratio are strongly dependent on cluster size. The behavior is attributed to geometric effects, suggesting that dehydrogenation of ethane on cationic rhodium clusters has strong steric requirements.

Keywords: Rhodium; Ethane; Dehydrogenation; Gas phase; Cluster

1. Introduction

Most catalysts used in large volume applications are heterogeneous, with the reaction occurring on the catalyst's surface. Transition metals, with their multitude of oxidation states, are among the most important industrial catalysts, and understanding the mechanisms of catalytic processes on an atomic scale is a topic of considerable current interest. The activity of a catalyst does not only depend on its chemical composition, but also very critically on the detailed structure of its surface [1]. Small metal clusters, with their varied structures and varying degrees of coordinative saturation of the individual atoms, are therefore very useful models for the catalytic process [2–4].

In the present study, Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry was used to investigate the reactions of small cationic rhodium clusters Rh_n^+, $n = 1–23$ with C_2H_6. Rhodium metal has a number of advantages for investigating hydrocarbon reactions. It lies in the area of the periodic table where the elements are rather reactive towards hydrogen, but do not have a very high affinity to carbon [5]. Obviously, any catalytic process requires adsorption of the reactants on the metal surface, occurrence of its reaction and then desorption of the products. Metals which immediately and irreversibly react to metal carbide are of little interest from the point of view of chemical catalysis. A great advantage of rhodium is that, unlike other typical catalyst metals like palladium or platinum [6,7], it is monoisotopic. While for such elements, only one mass peak is observed for each cluster size, the signal for larger clusters of elements consisting of many isotopes will be progressively diluted into so many isotopic peaks, so as to make the spectra extremely complex and difficult to analyze and interpret.

Ethane reacts exothermically with gas phase transition metal ions only via single and double dehydrogenation [8], i.e., by loss of one or two H_2 molecules, respectively. Nothing seems to be known about its reactivity with gas phase transition metal cluster ions. The reactions of rhodium clusters, anionic, neutral and cationic with small molecules like CO, C_6H_6, CH_4, O_2 and NO have been studied previously [9–19]. More than a decade ago, Kaldor and co-workers [17] have used the laser vaporization technique to generate neutral rhodium clusters, and investigated their reactions with D_2, N_2 and CH_4, and more recently, the reactions of cationic Rh_n^+ species with D_2 were also studied. Our group has studied the reactions of cationic and anionic rhodium clusters with benzene [10,11], methane [9], carbon monoxide [13] and azidoacetonitrile [14]. Schwarz and co-workers showed

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that reaction of $Rh_2CH_2^+$ with NH_3 leads to carbide formation with $Rh_2C^+(NH_3)$ as product which mimics unwanted soot formation in the DEGUSSA process [18]. Ford et al. have observed formation of N_2 in the reactions of Rh_6^+ with NO [19].

Computationally, the structure and magnetism of neutral rhodium clusters was studied by Chien et al. [20,21] and Aguilera-Granja et al. [22]. The interaction of small rhodium clusters with CO, butadiene and benzene was investigated theoretically by Balasubramanian and co-workers [23–25].

2. Experimental and computational details

The experimental apparatus and techniques used were described previously [12,14]. Briefly, the studies are carried out on a commercial 4.7 T Bruker/Spectrospin CMS47X FT-ICR mass spectrometer with an infinity cell and APEX III data station. The instrument has been fitted with an additional stage of differential pumping, providing a source chamber with a pulsed, supersonic expansion molecular beam source. The rhodium clusters were produced by laser vaporization [26–28] of the metal disk in the presence of a high pressure (20 bar) helium carrier gas. In the process of sample cooling and adiabatic expansion, not only neutral, but also positively charged clusters are formed. The cationic clusters are accelerated along the field axis of the superconducting magnet through several stages of differential pumping, decelerated and trapped in the ICR cell. The reactant gas, ethane, can be admitted to the instrument via adjustable leak valves. To study the bimolecular ion–molecule reactions, the pressure inside the ICR cell was raised from the base value from around 2×10^{-10} to 1.3×10^{-8} mbar by controlled admission of the ethane reactant gas. Commercially available C_2H_6 (99.95%, Messer–Griesheim) was used without further purification. Mass spectra were measured after varying reaction times. The relative rate constants for the first reaction step were obtained by fitting the observed time dependence of the parent and product cluster ion intensities, assuming pseudo-first order kinetics, and converted to absolute rate constants. Due to a leak in the gas inlet system, air was present in the UHV at a partial pressure of $\sim 1 \times 10^{-9}$ mbar, which did not interfere with the reactions. However, it introduces an uncertainty in the ethane pressure of 10%. Together with the uncertainty of the pressure measurement of 25% [29], the absolute rate constants carry a systematic error of 35%. The only reaction product observed from the air impurity was O_2 adsorption, which was accounted for in the kinetic analysis. Otherwise, the impurity did not interfere with the experiment.

3. Results and discussion

Preliminary experiments have shown that, consistent with previous experience with rhodium, the reactions do not lead to cluster fragmentation, i.e., to a loss of rhodium atoms. Therefore, an entire distribution of cluster sizes was studied simultaneously, without the need for mass selection. The clusters produced in the source were trapped in the ICR cell, and typically accumulated over 20 pulses of the vaporization laser. The mass spectra were then acquired after varying reaction delays, beginning with 0 s, which means immediately after the completed accumulation. Since in the course of the experiment, the pressure in the cell remains constant, the clusters react already during the accumulation time, so that even in the mass spectra corresponding to nominally zero reaction times, some reaction products are observable.

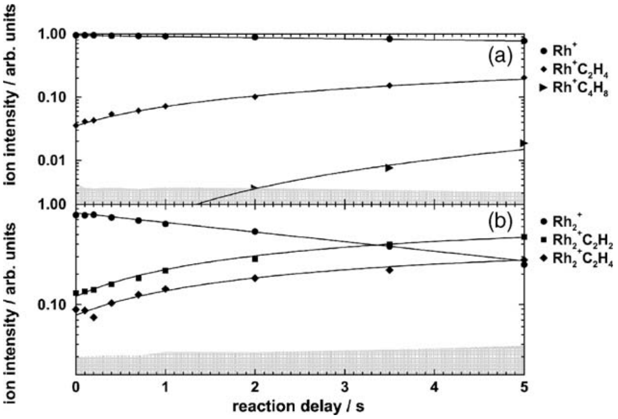

Fig. 1. Time dependence of the reaction of Rh^+ (a) and Rh_2^+ (b) with about 9×10^{-9} mbar of ethane. Note the unique primary product, $RhC_2H_4^+$ (squares) in the former, and two parallel products $Rh_2C_2H_4^+$ (diamonds) and $Rh_2C_2H_2^+$ (squares) in the latter case. Gray shaded areas denote the noise level.

The results are exemplified in Fig. 1a by the monatomic Rh^+ data, and in Fig. 1b by the diatomic Rh_2^+ data. In Fig. 1a, plotted on a semi-logarithmic scale, one can note over the first 5 s an exponential decay of the Rh^+, with a concurrent growth of the reaction product, which is identified as $RhC_2H_4^+$. At longer time, the growth of a second product, $RhC_4H_8^+$, can be detected. In Fig. 1b, one observes a considerably faster decay of the more reactive Rh_2^+ dimer ion and growth, in this case of two new mass peaks, both behaving as primary products. These can again be, based on exact measurement of their mass, unambiguously identified as $Rh_2C_2H_2^+$ and $Rh_2C_2H_4^+$.

The individual data points in Fig. 1 represent the normalized intensities of the Rh_n^+ reactant ions and of the reaction products. The thin lines shown in the figure represent then the theoretical fit to the experimental intensity data. With the help of similar fits like those exemplified in Fig. 1, one can derive the relative reaction rates and branching ratios for various sizes of clusters. All clusters in the range of $1 \leq n \leq 23$ were investigated in this way. Usually, different source conditions are needed to produce small or very large clusters, and it was therefore not possible to produce simultaneously adequate intensities of clusters over this entire range. The relative rates derived from the fit and presented in Fig. 2 are the result of three different experiments involving three overlapping ranges of cluster sizes. For all the experiments, a constant pressure of 1.3×10^{-8} mbar was maintained in the ICR cell. All the clusters react by the same two reactions exemplified already for $n = 1$ and 2 in Fig. 1, i.e., by partial dehydrogenation with the loss of one or two molecules of hydrogen:

$$Rh_n^+ + C_2H_6 \rightarrow Rh_nC_2H_4^+ + H_2 \qquad (1)$$

$$Rh_n^+ + C_2H_6 \rightarrow Rh_nC_2H_2^+ + 2H_2 \qquad (2)$$

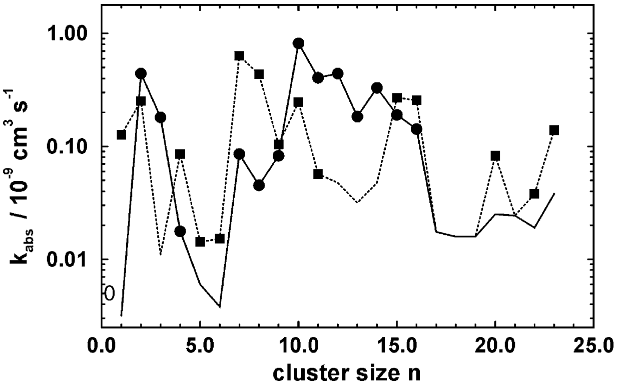

Fig. 2. Absolute rate constants for the first reaction step of the two primary reactions (1), formation of $Rh_nC_2H_2^+$ (circles and solid line) and (2), formation of $Rh_nC_2H_4^+$ (squares and dotted line). Lines without data points indicate the upper limit for reactions which were not observed.

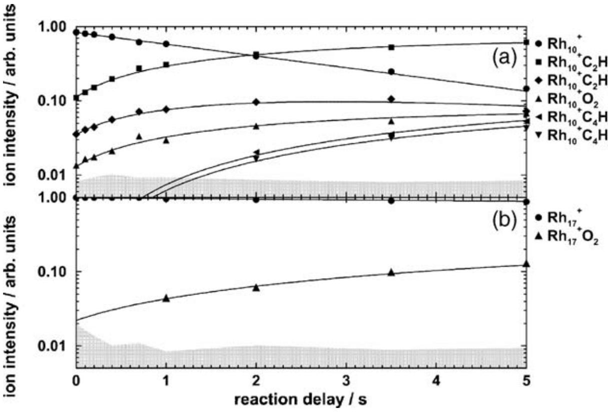

Fig. 3. (a) Reaction of the most reactive Rh_{10}^+ cluster, and the growth of three parallel primary products, corresponding to reactions (1), (2) and (3), $Rh_{10}C_2H_4^+$ (diamonds), $Rh_{10}C_2H_2^+$ (squares) and $Rh_{10}O_2^+$ (triangles) and (b) Rh_{17}^+ is unreactive towards ethane, but reacts efficiently with O_2, forming the product $Rh_{17}O_2^+$.

Starting with the $n = 6$ cluster, an additional product appears, corresponding to an increase in mass of 32 amu. This is clearly due to the addition of molecular O_2 onto the cluster, reaction (3), due to the small amounts present in the reaction gas:

$$Rh_n{}^+ + O_2 \rightarrow Rh_nO_2{}^+ \tag{3}$$

Since the exact concentration of the molecular oxygen is not known, its reactions are not discussed further. However, it has to be included in the kinetic analysis, otherwise the normalization of the total ion intensity would become incorrect. The presence of three parallel reactions (1), (2) and (3), and the presence of three primary products is exemplified for the fastest reacting cluster $n = 10$ in Fig. 3a. The overall reaction rates with ethane, as well as the branching ratios between reactions (1) and (2), show wild fluctuations from size to size. As shown for the $n = 17$ cluster in Fig. 3b, even those clusters which do not react with ethane at all, or to be more precise, whose reactions are presumably too slow to be detected in the present experiments, show an undiminished reactivity towards oxygen.

Table 1 lists values for the absolute rate constants, as well as reaction efficiencies as the ratio of the experimental rate constant and theoretically calculated collision rate constants from the surface charge capture (SCC) model [30], which is a modification of average dipole orientation (ADO) theory [31,32] to account for the finite size of the cluster. Since two ill-defined scaling factors go into the absolute rate constant, namely the

Table 1
Absolute bimolecular rate constants k_{abs}, collision rate constants calculated with the surface charge capture model k_{SCC} and efficiencies $\Phi_{SCC} = k_{abs}/k_{SCC}$

Cluster size, n	k_{SCC} (10^{-9} cm^3 s^{-1})	$Rh_nC_2H_2^+$		$Rh_nC_2H_4^+$	
		k_{abs} (10^{-9} cm^3 s^{-1})	Φ_{SCC} (%)	k_{abs} (10^{-9} cm^3 s^{-1})	Φ_{SCC} (%)
1	1.44	<0.003	<0.2	0.127	8.8
2	1.47	0.443	30.2	0.253	17.3
3	1.51	0.180	11.9	<0.011	<0.7
4	1.56	0.018	1.2	0.085	5.4
5	1.61	<0.006	<0.4	0.014	0.9
6	1.65	<0.004	<0.2	0.015	0.9
7	1.68	0.085	5.0	0.633	37.6
8	1.72	0.045	2.6	0.437	25.4
9	1.76	0.082	4.7	0.104	5.9
10	1.79	0.817	45.7	0.247	13.8
11	1.82	0.405	22.3	0.057	3.1
12	1.85	0.443	24.0	<0.047	<2.5
13	1.88	0.184	9.8	<0.032	<1.7
14	1.90	0.329	17.3	<0.047	<2.5
15	1.93	0.190	9.8	0.269	13.9
16	1.95	0.142	7.3	0.256	13.1
17	1.98	<0.017	<0.9	<0.017	<0.9
18	2.00	<0.016	<0.8	<0.016	<0.8
19	2.03	<0.016	<0.8	<0.016	<0.8
20	2.05	<0.025	<1.2	0.082	4.0
21	2.07	<0.024	<1.2	<0.024	<1.2
22	2.09	<0.019	<0.9	0.038	1.8
23	2.11	<0.038	<1.8	0.139	6.6

sensitivity of the ion gauge and the so-called geometry factor, which accounts for the position of the ion gauge relative to the ICR cell, together with the unknown impurity pressure the absolute values are probably reliable within 35%, while the relative rate constants have an error below 10%.

An examination of the rhodium cluster reactions with ethane becomes particularly interesting and revealing, when compared with the reactions with CO. While the Rh_n^+ clusters with $n = 1$–3 react very slowly with CO, they exhibit quite sizeable reactivities with the ethane. Even more interestingly, unlike the CO addition, which above a threshold around $n = 10$ shows only mild variations in rates, both the rates of the reaction with ethane, as well as the branching ratios between reactions (1) and (2) exhibit wild fluctuations as a function of the cluster size, n. Already the monatomic cation reacts with ethane according to (1), with the loss of an H_2 molecule. The diatomic cluster, Rh_2^+, exhibits both reactions (1) and (2), while for $n = 3$ exclusively, loss of two hydrogen molecules is observed. The $n = 4$ cluster reverts to both reactions, but with a relatively low rate, while for the $n = 5, 6$, only $Rh_nC_2H_4^+$ is formed to a small extent. All clusters between $n = 7$ and 11 exhibit both reactions (1) and (2), but with varying rates and reversing branching ratio. The $n = 7$ and 8 react fairly efficiently with the loss of one H_2, while double dehydrogenation dominates for the $n = 10$–14 clusters. The Rh_9^+ cluster is relatively unreactive, exhibiting small and comparable rates for both reactions. For clusters $n = 15$, 16, 20, 22 and 23, single dehydrogenation dominates, with only $n = 15, 16$ showing some degree of double dehydrogenation according to (2). The clusters with $n = 17$, 18, 19 and 21 are largely unreactive towards ethane.

The products of the primary reaction may react with a second molecule of ethane to form secondary products. A quantitative analysis of these secondary reactions was not possible with the signal to noise level in the present experiment. A qualitative analysis shows that even here considerable variations from one cluster size to another occur. Thus, already the product of the primary reaction of the monatomic rhodium cation, $RhC_2H_4^+$ reacts again with the elimination of one H_2 molecule, forming an $RhC_4H_8^+$ product:

$$RhC_2H_4^+ + C_2H_6 \rightarrow RhC_4H_8^+ + H_2 \qquad (4)$$

On the other hand, the $n = 7$ cluster, for which the dominant first step reaction also was the elimination of a single hydrogen molecule, eliminates two H_2 in the secondary reaction:

$$Rh_7C_2H_4^+ + C_2H_6 \rightarrow Rh_7C_4H_6^+ + 2H_2 \qquad (5)$$

The most reactive $n = 10$ cluster forms relatively slowly two secondary products, $Rh_{10}C_4H_4^+$ and $Rh_{10}C_4H_6^+$, but in this case, the secondary reactions are more difficult to untangle reliably, since the cluster forms two primary products according to both reactions (1) and (2). It appears, though, that the minor primary product, $Rh_{10}C_2H_4^+$ must make a significant contribution, since its concentration goes quite rapidly through a maximum, and beyond about 3 s decreases again, as can in fact easily be seen in Fig. 3a, indicating that it is rather efficiently reacting away. Quite interesting is the case of the $n = 15$ cluster, which rather reluctantly dehydrogenates ethane to an $Rh_{15}C_2H_4^+$ primary product. This, however, apparently reacts in a secondary reaction with the elimination of three hydrogen molecules so efficiently, that after 5 s, the $Rh_{15}C_4H_4^+$ ion is already the most abundant product:

$$Rh_{15}C_2H_4^+ + C_2H_6 \rightarrow Rh_{15}C_4H_4^+ + 3H_2 \qquad (6)$$

Mainly the clusters between 7 and 11 react efficiently with ethane in a secondary reaction with elimination of one or two hydrogen molecules, but the $Rh_nC_4H_4^+$ complex was observed only for $n = 10$, 15 and 16.

The relatively high dehydrogenation efficiencies for a saturated hydrocarbon like ethane seem to be somewhat at odds with the conclusions of previous investigations, for instance, the trailblazing studies of El-Sayed and co-workers [33,34] who concluded that at least one double bond is required for the dehydrogenation of hydrocarbons on niobium clusters. In reactants containing double or triple bonds, a relatively strong interaction of the π-orbitals with the metal atoms can take place, the cluster–ligand interaction potential is deep and the density of internal states near the dissociation limit is high, which increases the probability for the formation of a long-lived collision complex, which eventually reacts. Complexes between monatomic ions or ionic metal clusters, and benzene or other unsaturated compounds can form readily even in the ultra high vacuum, effectively collision-free environment of the ICR instrument by radiative association [10,35,36].

With ethane as a saturated hydrocarbon, no stable binary complex $Rh_nC_2H_6^+$ has been detected. However, the reaction probabilities for some cluster sizes are quite high, which indicates that the C—H bond activation must proceed efficiently and with a relatively low barrier for certain cluster sizes, which most likely depends on the details of the topography of the metal surface. Overall, one observes that above $n = 16$, the reactivity is greatly reduced, and only a few clusters still exhibit dehydrogenation reactions. This trend may represent the increasing coordinative saturation of the metal atoms with the increasing size of the cluster. The reactive sizes probably represent clusters with specific structural features, like ad-atoms or holes. In addition, the effective temperature of the collision complex decreases with size, which reduces the probability that the barrier for dehydrogenation is overcome, as discussed previously [3]. Unfortunately, there is no experimental information about the structure of rhodium clusters, and also quantum chemical computations of the geometry and other properties of species containing more transition metal atoms is still a very challenging problem. Clearly, a thorough computational study of the structure of at least small ionic clusters is of considerable interest.

In view of the considerable reactivity of cationic rhodium cluster with ethane found here, it is of interest to compare the present results with earlier studies of the their reactions with methane [9,17]. In those studies, it was shown that with the exception of Rh_2^+ which reacts with methane with H_2 elimination and carbene formation, all the other “naked” cationic Rh_n^+ clusters were found to be completely unreactive. Interestingly, however, when one forced the reactants to form a long-lived complex by ligand exchange reactions between cold $Rh_n{}^+Ar_m$ clusters and methane, also $Rh_3{}^+$ was found to react, yielding the dehydrogenated $Rh_3CH_2{}^+$ product. In the present case, instead of the complex being stabilized by ligand exchange, the additional degrees of freedom, and in particular, the presence of the low barrier internal rotation in ethane, and its presumably higher binding energy as compared to methane, might be responsible for extending the time scale of the collision, and making a reaction possible.

When the C_2H_6 molecule adsorbs on the cluster, the binding energy may heat the cluster sufficiently to overcome the barrier for the dehydrogenation reaction. The sharply decreasing reaction rates for large rhodium clusters may also be due to the fact that as the cluster becomes larger, the temperature rise resulting from the adsorption of the reactant will become progressively smaller, reducing the probability that the barrier to reaction can be overcome [3]. For large clusters, the adsorption of C_2H_6 on a reactive site seems to become unfavorable, and the collision complex back-dissociates before the reaction can occur. The reason for the wild fluctuations would be the specific geometry of a certain cluster size.

4. Conclusions

In the present work, cationic rhodium clusters, $Rh_n{}^+$, $1 \leq n \leq 23$ were generated and their reactions with ethane as a function of cluster size were investigated in an FT-ICR mass spectrometer under binary collision conditions. Overall, the reactivity of rhodium clusters towards ethane depends strongly on the cluster size. The primary products consist in dehydrogenation with loss of one or two H_2 molecules for almost all the clusters, the most reactive rhodium cluster being $n = 10$. $Rh_5{}^+$ and $Rh_6{}^+$ exhibit a reactivity minimum with ethane, and the larger sizes $n = 17$–19 and 21 are completely unreactive. It is suggested that geometric effects determine the reactivity of rhodium clusters towards ethane.

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