

Mechanisms of catalytic dehydrogenation of alkanes by rhodium clusters Rh_n^+ probed by isotope labelling

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Dedicated to the memory of Chava Lifshitz.

Abstract

The regioselectivity for the dehydrogenation of alkanes by rhodium clusters was investigated by reacting Rh_n^+ , $n = 1\text{--}20$, with the isotopically labelled alkanes ethane-1,1,1- d_3 and propane-1,1,1,3,3,3- d_6 . For Rh^+ reacting with propane a clear preference for a 1,2- over a 1,1- and 1,3-mechanism was observed. For larger clusters, hydrogen scrambling is faster than hydrogen elimination, which essentially leads to statistical formation of the neutrals H_2 , HD, and D_2 . Isotope scrambling with D_2 was also used as a structural probe for the reaction products of rhodium clusters with ethane. The intactness of the C–H bonds was demonstrated for ($n > 6$). The studies are completed with a detailed kinetic analysis for the reaction of Rh_7^+ with ethane and ethane/hydrogen and ethane/helium mixtures. An over-all picture with efficient C–H bond activation and fast and reversible hydrogen rearrangements emerges on the basis of these experiments. Some of the dehydrogenation reactions appear to be reversible. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Catalytic dehydrogenation of alkanes to alkenes is an important process, which provides the feedstock for a large fraction of the polymer industry [1]. Since alkane dehydrogenation usually is a significantly endothermic process, the process requires either oxidation of the products, in particularly H_2 , or the supply of thermal energy. It will be of great interest to better understand the mechanisms of dehydrogenations in general, and to suggest new catalysts for the industry in particular. In this respect, the study of gaseous transition metals and gaseous transition metal clusters is valuable [2–6]. Further insights are gained by directly comparing the behaviour of gaseous and supported atoms and clusters, as demonstrated for instance for rhodium in catalysing the trimerisation of acetylene [7]. Numerous experimental studies on rhodium cations [8–14] and rhodium clusters [15–17] as well as theoretical calculations [18–20] have aimed in understanding the principles for dehydrogenation of hydrocarbons, in particular alkanes. The metal clusters mimic essential features

of catalyst surfaces. At the same time we also have to realize the differences. While a small gas phase metal cluster is an isolated system, metal clusters on a catalyst surface are in thermal contact with the solid support. While reaction products thermally desorb from a bulk surface, they have to be liberated from a gas phase cluster by activation (e.g., collisional activation). Despite the differences, gas phase cluster chemistry gives unique insights into important elementary reaction steps, including complications like cluster decomposition (reconstruction of the catalyst) and complete dehydrogenation (coking).

We have recently reported on the dehydrogenation of alkanes by cationic rhodium clusters [21]. Besides a surprising consistency in the cluster-size/reactivity pattern, it was also observed that dehydrogenation on gaseous rhodium clusters did not occur to completion, but for many reactions the generation of formal cluster-alkene adducts $(\text{Rh}_n\text{C}_m\text{H}_2\text{m})^+$ was observed. Our earlier experiments did neither reveal details about the structure of the alkene adducts nor their mechanism of generation. The thermodynamically most stable dehydrogenation products of propane and ethane are propene and ethene, respectively. Despite this, the actual mechanism for dehydrogenation is not necessarily via a 1,2- H_2 elimination mechanism. A preference of carbene binding to π binding may for example induce a shift in mechanism

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from 1,2 to 1,1. The use of isotopically labelled molecules can provide these details.

In this context the principal issues are the structure of the intermediates and the regioselectivity of dehydrogenation. For atomic transition metal ions, regioselectivity is known to be strongly dependent on the nature of the metal, e.g., dominant 1,4-dehydrogenation for the reaction of Co^+ with *n*-butane in contrary to dominant 1,2-dehydrogenation for Rh^+ [9–11,22,23]. In case of metal clusters it may be possible that the mechanism of dehydrogenation is not only governed by the element, but also by the number of metal atoms. We have recently investigated the dehydrogenation of alkanes by rhodium clusters. While cationic rhodium clusters readily dehydrogenate higher alkanes, methane is less reactive. Without additional excitation, only Rh_2^+ and Rh_3^+ are capable of activating methane. The latter even requires the assistance of an inert chaperon such as argon to achieve the 1,1-dehydrogenation [16]. The reason for a higher reactivity of the higher alkanes compared to methane could either be due to a different mechanism or due to the possible formation of more stable alkene intermediates compared to carbene like species which is required in case of methane.

In this study, ethane-1,1,1- d_3 and propane-1,1,1,3,3,3- d_6 have been chosen as model substrates to probe the regioselectivity of dehydrogenation by rhodium clusters Rh_n^+ , $n = 1$ –20. In addition, isotope exchange experiments were performed to probe for the structure of reaction intermediates and for reversibility.

2. Experimental

The experiments were performed with a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer, Bruker Apex 47e (Bruker Daltonics, MA, USA), with a supplementary source chamber with additional pumping attached to the standard source chamber. The experimental set-up is of the same design as used by Berg and co-workers, and has already been described thoroughly [21,24,25]. Thus, only a brief description of the operational techniques and conditions used in the present study will be given.

Rhodium cluster cations were generated by pulsed laser vaporisation of a rotating rhodium disk (99.9%, Goodfellow Cambridge Ltd., UK). A hot plasma was produced by focusing the second harmonic (532 nm) of a PL8020 Nd:YAG laser (Continuum, CA, USA, 20 Hz, 6–12 mJ per 5 ns pulse, focusing spot size 0.1–0.2 mm) on the target. The plasma was subsequently cooled and clustered by co-expansion with a short pulse of helium carrier gas through a confining channel (35, 2 mm i.d.). The helium gas (99.9999%, Aga, Norway) was introduced via a custom-built piezoelectric valve (20 μs opening time, backing pressure 30–40 bar). Both ions and neutrals are made in the process, making further ionisation unnecessary. The cluster ions were accelerated downstream from a 410 μm skimmer, transferred into the high field region of the 4.7 T superconducting magnet, decelerated and trapped in the ICR-cell. To increase the signal intensity, rhodium clusters were accumulated by 20 repetitive cluster generation and transfer cycles.

Hydrogen (99.97%, Aga, Norway), deuterium (99.998%, Hydro Gas, Norway), methane- d_4 (99 atom%, CDN Iso-

topes, Canada), ethane (99.9%, Aga, Norway), ethane-1,1,1- d_3 (99 atom%), propane-2,2- d_2 (99 atom%), and propane-1,1,1,3,3,3- d_6 (98 atom%, all Icon Isotopes, USA) were dispensed into the FT-ICR cell through a leak valve. During the experiments the pressure in the cell was raised from the base value of $\sim 3 \times 10^{-10}$ mbar to partial pressures of the hydrocarbons estimated to approximately 5×10^{-9} to 5×10^{-8} mbar. The substrate pressure was read out by means of a cold cathode ion gauge which was calibrated using the reaction of $\text{NH}_3^{\bullet+}$ (generated externally by EI) + $\text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NH}_2^{\bullet}$, $k = 2.2 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [26] and corrected by relative sensitivity factors of $R(\text{NH}_3) = 1.12$, $R(\text{He}) = 0.37$, $R(\text{H}_2) = 0.59$, $R(\text{CH}_4) = 1.23$, $R(\text{C}_2\text{H}_6) = 1.91$, and $R(\text{C}_3\text{H}_8) = 2.56$ [27].

Reaction rates were determined directly from the total cluster distributions without prior isolation. The time dependent product ion distribution was obtained by recording mass spectra after a variable reaction time, t_r . Pseudo-first-order bimolecular rate constants for the total consumption of the rhodium cluster cations were taken from the slope of the straight lines obtained by plotting the natural logarithm of the normalized cluster ion intensities against t_r . The intensities were normalized against the total sum of ion intensities pertaining to each specific reactant cluster. Independent experiments with isolated cluster cations (correlated frequency sweeps [28] and in some cases additional single frequency shots) confirmed that there was no interference with potential decomposition products from larger clusters under the given experimental conditions. However, some decomposition products were observed at long reaction times (>60 s) and at high alkane pressures ($> 2 \times 10^{-7}$ mbar). The major decomposition product was Rh_2C_3^+ irrespective of the carbon source, but the significant loss of ions from the cell under these conditions impedes a detailed analysis of the decomposition reaction [21].

The uncertainty of the absolute rates is typically $\pm 40\%$, but relative rates are very precise. Errors are given at the 95% confidence level. For the determination of rate constants, reactions were observed until 90% consumption of the parent cluster ion. Relative partial rates for the primary products were determined by observing the reactions until 10% of secondary products (reaction with a second alkane) or oxidation products had formed and a simplified kinetic model with an average rate, k_{avg} , for the reaction rates of the primary to the secondary products was employed. The main difficulty for slow reactions was the competing reaction with molecular oxygen present in the background of the cell, which hampered the assignment of the reaction chronology for product clusters containing oxygen and hydrocarbon. Entries of slow reactions are therefore missing in Tables 1 and 2. Theoretical collisional rates were obtained using the parameterised model of Su and Chesnavich [29].

3. Results and discussion

As already mentioned, ethane dehydrogenation may occur via 1,2-elimination mechanism (Horiuti-Polanyi mechanism [30]) or a 1,1-elimination mechanism. This general situation is illustrated in Scheme 1. In principle each step may be reversible. The purpose of the present work is to probe to which extent this is true. For propane, the additional 1,3-elimination pathway may

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