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Methane activation by platinum cluster ions in the gas phase: effects of cluster charge on the Pt₄ tetramer

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Abstract

The reactions of cationic and anionic platinum clusters Pt_n[±], $n = 1 - 9$, with methane CH₄ are investigated under single collision conditions in a Fourier-Transform Ion Cyclotron Resonance Mass Spectrometer. The reaction of the platinum clusters proceeds through the activation of C–H bonds of methane and leads to the subsequent elimination of molecular hydrogen H₂ to form the final metal–carbene complex Pt_n[±]CH₂. The cation cluster reactions proceed in general with collision rate whereas the anion cluster reactions are more than an order of magnitude slower. The platinum tetramer anion is unique among all the clusters studied, reacting more efficiently than the corresponding cation. Tentative interpretation in terms of electronic and geometric effects is performed. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The ability of transition metals to activate the relatively unreactive C–H and C–C bonds of alkanes makes them useful catalysts in many industrially important chemical reactions and is one of the main reasons motivating the recent interest in studies of metal atoms and cluster reactions. Particularly interesting from the practical point of view appear the transition metals of the 5d series. C1 chemistry and functionalization of methane is of considerable tech-

nical interest, and it was recently shown by Irikura et al. [1,2] that, unlike the 3d and 4d elements, the cations of the 5d series are able to exothermically dehydrogenate methane.

It may however, be noted that although the second-row transition metal cations are unreactive towards methane, we have recently shown that the same does not hold for clusters, and the rhodium dimer Rh₂⁺ reacts efficiently with the loss of hydrogen [3]. Small transition metal clusters and their ions are attractive model systems for studies of heterogeneous catalysis, since they can be treated more easily computationally than bulk surfaces; promising multi-reference-CI calculations on Rh_n⁺, $n = 3-5$, were reported by Majumdar and Balasubramanian [4].

The neutral Pt_n clusters with $n \leq 24$ were investigated in a chemical fast flow reactor [5] and found to dehydrogenate methane yielding Pt_nC_{1,2}H_y prod-

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ucts. They exhibited a decreased degree of dehydrogenation with cluster size, and a sudden reactivity drop for clusters with six or more atoms. The reactions of the Pt^+ cation were recently investigated both theoretically and experimentally by Siegbahn, Schwarz and coworkers [6,7] and in our group [8]. Schwarz et al. concluded that the atomic cation catalyzes the oxidation of methane by molecular oxygen to yield methanol, formaldehyde and higher oxidation products. The insertion of the platinum cation into one of the C–H bonds of methane takes place via an electrostatically bound transition state [8] to form an hydrido–methyl–platinum complex, being the overall minimum on the potential energy surface. Migration of a second hydrogen atom leads to subsequent elimination of molecular hydrogen. Weisshaar and Blomberg [9] reported measurements of effective bimolecular rate constants for neutral ground-state Pt ($5d^96s$) with methane and carried out quantum chemical calculations on the PtCH_4 system using the parametrized configuration interaction method PCI-80. As in the cationic case, the path leads from $\text{Pt} + \text{CH}_4$ to the C–H bond insertion intermediate and onward to elimination of H_2 . But in contradiction to the cationic platinum the calculations make a clear prediction that the product is the collisionally stabilized, long-lived HPtCH_3 insertion complex rather than the carbene complex, separating the insertion product from the elimination products, which are in any event substantially endothermic from ground state $\text{Pt} + \text{CH}_4$, with a large barrier.

Unlike the neutral species, the corresponding cluster ions have thus far not been studied. Our Fourier Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometer equipped with a versatile external molecular beam cluster source permits us to investigate both anionic and cationic transition metal clusters with up to fifty atoms under single collision conditions. Comparisons of the reactions of metal cluster anions and cations under otherwise identical conditions should be quite informative. While in the limit of bulk metals the properties such as surface reactivity, work function, magnetism, geometry, or band structure should be little affected by the shortage or excess of a few electrons, there are tremendous differences between the ionization potential and other physical properties of a metal cation, neutral atom, and the corresponding anion. While the ques-

tion of how quickly these properties converge as a function of size is a fascinating problem for chemists and physicists [10–18] the number of studies permitting direct comparison of anion and cation reactivities has thus far been quite limited [19–21].

2. Experimental

Our apparatus was described previously [22]. A commercial FT-ICR mass spectrometer (Spectrospin CMS47X) with a 4.7 tesla magnet was equipped with a 60 mm cylindrical ‘infinity’ cell [23] and fitted with a separate differentially pumped chamber allowing the use of external molecular beam ion sources. The clusters are produced by laser vaporization [24,25] of rotating platinum foil (Aesar 99.99%, 10 Hz, 5 ns Pulsed Nd-YAG, 532 nm, 15 mJ). The initially produced plasma is entrained in a pulse of helium carrier gas (10–25 bar, 50 μs) from a home-built piezoelectric valve, whose opening is synchronized with the laser pulse. The clusters form in a confining flow channel (35 mm, 2 mm i.d.) and are further cooled by an adiabatic supersonic expansion into high vacuum.

The cluster ions, produced directly in the vaporization source without postionization, were accelerated downstream from a 1 mm skimmer, transferred into the high field region of the superconducting magnet, decelerated, and stored inside the ICR cell. Switching between anions and cations is accomplished by changing the polarity of the ion transfer optics.

To study the bimolecular cluster ion–molecule reactions the pressure inside the ICR cell was raised from the base value of around 2×10^{-10} mbar to about 5×10^{-8} mbar by controlled admission of methane. Commercially available methane (Messer-Griesheim, 99.5%) was used without further purification. Mass spectra of the cluster distribution and their products were taken after varying reaction delays. Relative rate constants were then extracted from the temporal changes in the intensities of the initial clusters and their products by assuming pseudo first order reaction kinetics. Absolute rate constants were derived from scaling the relative rates with the accurate pressure in the cell region.

3. Results and discussion

The existence of six stable isotopes leads to the appearance of complex multiplets in the mass spectra of the platinum clusters and their reaction products. This naturally dilutes significantly the signal and makes data analysis more difficult, and explains why we had to limit the present study to clusters with $n \leq 9$ atoms, even though we could easily investigate clusters of monisotopic metals like Nb or Rh to $n > 50$. The data are exemplified by the Pt_5^+ cation in Fig. 1, with the points indicating the experimental intensities, and solid lines the results of a kinetic fit. The primary reaction product, Pt_5^+CH_2 , is found to react with another methane molecule to form $\text{Pt}_5^+\text{C}_2\text{H}_4$ in the second reaction step, with one H_2 molecule being lost each time. A third reaction step occurs without H_2 loss, resulting in a tertiary $\text{Pt}_5^+\text{C}_3\text{H}_8$ product. The primary dehydrogenation re-

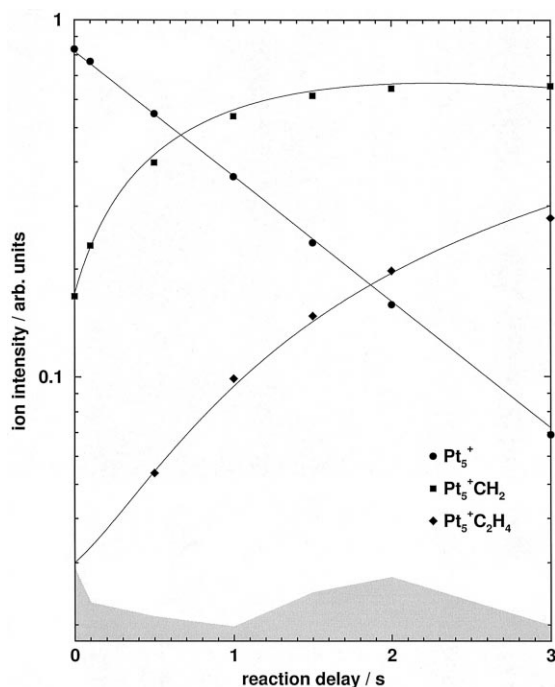


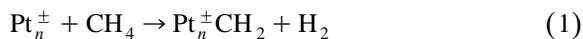
Fig. 1. Time profile for the reaction of size selected Pt_5^+ with CH_4 . The experimental data (solid points) are fitted to an unbranched consecutive two-step reaction assuming pseudo first-order kinetics (solid lines).

Table 1

Absolute rate constants for reaction (1), all values in $10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$

Pt_n	k^{abs} cations	k^{abs} anions
1	46 ± 2.9	< 0.04
2	70 ± 5.7	2.3 ± 0.4
3	87 ± 7.1	3.0 ± 0.9
4	2.7 ± 0.7	17 ± 2.5
5	110 ± 13	7.2 ± 0.9
6	130 ± 14	< 0.17
7	110 ± 16	6.8 ± 1.7
8	97 ± 14	< 0.76
9	110 ± 10	< 0.59

action step for all the clusters studied, anions and cations is:



The relative rate constants extracted by fitting the data for the cluster cations in the size range $n = 1$ –9 and converted to absolute rate constants k^{abs} , are summarized in Table 1. Using the known neutral reactant gas densities, one can calculate the collision rates according to average dipole orientation k^{ADO} [26] and convert them to absolute reaction efficiencies, $\phi = k^{\text{abs}}/k^{\text{ADO}}$, plotted as the open symbols in Fig. 2. Obtaining for larger clusters efficiencies with slightly more than 100%, the most reactive peak ($n = 6$) is set to 100% and all others are scaled to this value. One finds that the reactions are fast, approaching 100% for most naked platinum cluster cations. One notable exception is the $n = 4$ cluster, whose reactivity is more than an order of magnitude lower.

The data for the anions were obtained under identical conditions, and analyzed in the same way, and are for comparison also plotted as the solid symbols in Fig. 2. In agreement with our observations for small niobium clusters [21], one can see that the reactivities of most of the anions are about an order of magnitude lower than those of the cations. A quite prominent exception is again the $n = 4$ cluster. In contrast with the cation, whose reactivity represented a deep minimum, the Pt_4^- tetramer is the most reactive of the anions studied, and stands in fact alone in reacting considerably more efficiently than the Pt_4^+ cation.

Structure and energetics of the platinum cation have been the subject of several detailed theoretical

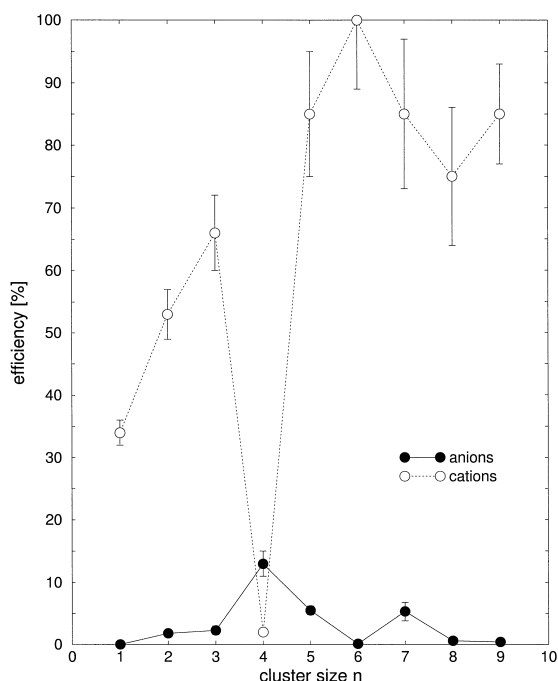


Fig. 2. Efficiencies for the reaction of methane with cationic (open circles) and anionic platinum clusters (filled circles) Pt_n^\pm , $n = 1-9$.

investigations at various levels of theory [6–8]. Density functional calculations suggest, that the dehydrogenation of methane proceeds via a hydrido-methyl-platinum global minimum on the potential surface with an almost negligible barrier between the electrostatically bound Pt^+CH_4 complex and the inserted hydrido-methyl structure HPt^+CH_3 [8]. In spite of the deceptively simple appearance of Eq. (1), the reaction pathway for clusters is undoubtedly relatively complex, and may involve several intermediates separated by activation barriers, shown in Fig. 3. Formation of an electrostatically bound cluster-methane complex may be followed by overcoming a barrier to an intermediate with probably a metal inserted into one of the C–H bonds, and eventually by decomposition of this intermediate and elimination of molecular hydrogen, H_2 . A potential resulting from ab initio calculations on the platinum monomer cation [7] appears to lack a barrier between the methane adduct and the inserted intermediate, but the situation may well be different for the usually less reactive larger clusters.

For monatomic Pt^+ reaction we find an efficiency of 47%, a result somewhat lower than the previous report of 80% [27], which may well be due to differences in pressure calibration. The increasing reactivities between $n = 1$ and 3 can be attributed to the easier formation of longer lived complexes for the polyatomic clusters. The relatively weak bond computed for the $n = 1$ Pt^+ complex [7,8] was rationalized by the fact that the Pt^+ excited state $5d^8 6s^1$ with three unpaired electrons can form only three covalent bonds. With two being required to bind the two hydrogens, only a single electron remains to bind the CH_2 group, resulting in a single σ bond and an unpaired electron at the carbon. In the larger species this extra electron may overlap with orbitals on other platinum atoms, form an additional σ bond, and thus stabilize the reaction intermediates and reduce the activation barriers.

The deep reactivity minimum and a precipitous efficiency drop to less than 3% of the collision rate for the specific Pt_4^+ cation is surprising. Our preliminary DFT calculations suggested a tetrahedral structure for Pt_4^+ , making it the smallest cluster where each platinum is coordinated to three other atoms. The higher coordination might increase the activa-

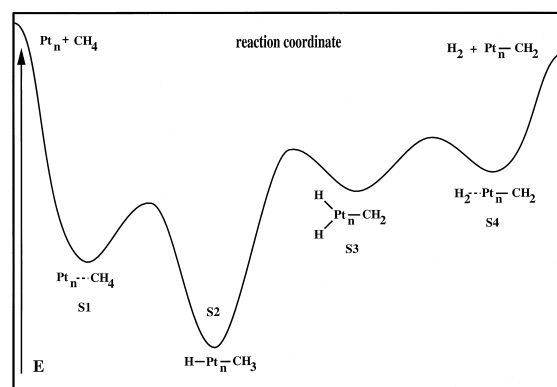


Fig. 3. Schematic view of the reaction path from $\text{Pt}_n^\pm + \text{CH}_4$ reactants to the observed $\text{Pt}_n^\pm \text{CH}_2 + \text{H}_2$ primary products. Formation of a complex with methane is followed by an insertion of the Pt atom or cluster into one of the C–H bonds of methane and formation and ejection of a molecular H_2 product. The assumed reaction surface involves molecular complexes $\text{Pt}_n^\pm \cdots \text{CH}_4$ and $\text{H}_2 \cdots \text{Pt}_n^\pm - \text{CH}_2$ of the metal cluster with the CH_4 reactant and the H_2 product, respectively, as well as the two covalently bound species with three activation barriers separating the four intermediates.

tion barriers along the reaction pathway, and result in the reduced reactivity. By a similar argument one might expect the degree of coordination to be further increased in a trigonal bipyramid $n = 5$ cluster, but it may be noted that recent calculations for Rh_5^+ have predicted a distorted structure with the fifth atom bridging a single Rh–Rh bond [4]. Should all the larger clusters contain atoms of low coordination, these might act as reaction centers explaining their high reactivity.

The catalytic efficiency of transition metals is based on their open-shell nature, and the resulting multitude of low-lying electronic states, and variety of reduction and oxidation processes. Alkanes are believed to form with metals ‘non-classical’ complexes of the type $\text{M} \cdots \text{CH}_4$ with a ‘three center two electron’ bond [28]. In such a complex the stable C–H bond is considerably weakened and lengthened, on one hand by donation of the CH binding σ electron pair into the empty orbitals on the metal (or metal cluster), and conversely by back-donation of the highest energy electrons from the metal into the CH antibonding σ^* orbital. Based on our computation [8], in the case of Pt^+ such a complex denoted as S1 in Fig. 3 represents only a very shallow minimum, if at all, separated by a very low barrier from the inserted S2 global minimum HPt^+CH_3 . The second step leads then over a substantial barrier to transfer of a second hydrogen to the metal, and formation over the methylene species $\text{H}_2\text{M} \cdots \text{CH}_2$ of an $\text{H}_2 \cdots \text{MCH}_2$ complex. This weakly bound complex then dissociates the adsorbed molecular hydrogen giving the final MCH_2 metal carbene product.

The pathway of this platinum insertion and dehydrogenation processes will obviously be strongly affected by the charge of the metal or metal cluster. The presence of a positive charge on the metal will clearly strengthen the interaction and enhance the effect of electron withdrawal. This is reflected in the calculated high $\text{Pt}^+ \cdots \text{CH}_4$ binding energy of about 126 kJ/mol, and the small activation barrier (2 kJ/mol) for the bond insertion in the case of the monomer [8]. The Pt^+ cation possesses a very low-lying excited state $5d^8 6s^1$ with three singly occupied orbitals, and is thus able to form the three covalent bonds needed to bind the hydrogen atoms and the methyl ligand (S3 in Fig. 3).

The opposite effects are to be expected for the negatively charged species. The platinum anion with the electronic configuration $5d^9 6s^2$ possesses only one unpaired electron, while three are needed to form the intermediate inserted S3 structure. Complete rehybridization with electron promotion from the 6s or 5d orbital into 6p orbital would be needed to form the inserted HPtCH_3 and $\text{HPtH}(\text{CH}_2)$ intermediates, and the activation energy will undoubtedly be high. The much more diffuse negative charge on the anions will, besides reducing the electron withdrawing effects, also less strongly polarize the ligand. These effects are evidenced by our observations that, similar to the previous studies of small Nb clusters [21], also the anions of platinum exhibit reactivities that are overall more than an order of magnitude lower than those of the cations.

The most striking feature of the anion reactions is again the anomalous reactivity observed for the tetramer. Pt_4^+ represents a sharp reactivity maximum, which exactly anticorrelates with the minimum observed for the cation, and contrary to the overall trend reacts more than a factor of six faster than Pt_4^+ . In our previous study of niobium clusters [21] we observed identical reactivity patterns for anionic and cationic clusters with $n \geq 19$ and argued that the reactivities and stability of larger clusters are influenced more by their geometric properties rather than by their electronic structures. In smaller clusters the electronic structure and geometry are not independent and will affect each other strongly. Adding or subtracting one electron in the case of the Pt_4 cluster drastically changes the electronic and thus possibly also the geometric structure.

As noted above, the preliminary DFT calculations yielded a tetrahedral structure for the tetramer cation. The high reactivity of Pt_4^+ could be understood if it has a considerably different geometry, with perhaps a planar structure.

4. Conclusion

Platinum cluster cations and anions with up to 9 atoms were generated, and their reactivities with methane investigated. The presence of a negative charge is found to greatly decrease the reaction efficiency. The tetramer cluster behaves quite

anomalously, with the cation representing a deep reactivity minimum, while the anion on the contrary exhibits a pronounced maximum in reactivity. We attribute this unusual behavior to drastically different geometries of the anion and cation tetramers.

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