Reactions of platinum clusters Pt$_n^\pm$, n = 1–21, with CH$_4$: to react or not to react

Christian Adlhart and Einar Uggerud*

The relative reactivity of any given neutral platinum cluster falls in-between that of the corresponding anion and cation.

One fascinating aspect of cluster chemistry is how reactivity and other properties vary with cluster size. Knowledge about size–reactivity relationships for different metals has become even more topical with the recent advent of practical techniques for soft-landing size-selected metal clusters on surfaces, eventually to be used as catalysts.[1] Platinum remains one of the most remarkable catalytic elements—in particular in connection with C–H activation—and deserves particular attention. We report the results of gas phase reactions between methane and platinum clusters (Pt$_n^\pm$, n = 1–21), both positively and negatively charged. Until now, this reaction has only been studied for cationic[2-4] clusters and anionic clusters with $n \leqslant 9$, in addition to a study of neutral clusters with $n \leqslant 25$.[5] Reactions were performed in the cell of an FT-ICR mass spectrometer.† The use of monoisotopic ^{195}Pt facilitated detection of larger clusters.

Fig. 1 is illustrative of the reactivity of the platinum clusters. Dehydrogenation is the only primary reaction observed.

$$Pt_n^\pm + CH_4 \rightarrow Pt_nCH_2^\pm + H_2 \qquad (1)$$
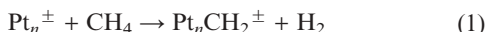
However, it is most noticeable that the reaction is either very efficient (for some clusters) or completely absent (for others). A majority of the cationic clusters with $n < 16$ reacts efficiently, and the same applies for the smaller anionic clusters ($n < 7$). Fig 2 shows the relative reaction rates as a function of the number of atoms. In some cases (n = 5–9 and 11), a secondary reaction according to

$$Pt_nCH_2^+ + CH_4 \rightarrow Pt_nC_2H_4^+ + H_2 \qquad (2)$$

was also observed for the cations.

The anionic trimer deserves special mention. The reaction between Pt$_3^-$ and methane does not proceed to completion. Our analysis of the kinetic data, in addition to ion isolation experiments, clearly demonstrates the existence of two electronic/geometric isomeric forms; one reactive (20%) and one unreactive.

All reactions were clean, unambiguous, free of branching products, and there was no evidence for products of methane addition (for n = 1–21). Slow formation of adducts with background O$_2$ was observed for $n > 10$, demonstrating significant oxygen affinity and also indicating that the cluster ions are

Department of Chemistry, University of Oslo, P. O. Box 1033 Blindern, N-0315 Oslo, Norway. E-mail: einar.uggerud@kjemi.uio.no; Fax: +47 22855441; Tel: +47 22855537
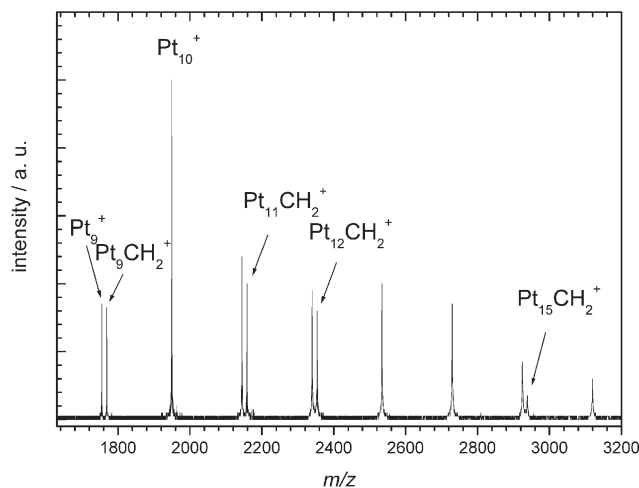

Fig. 1 Mass spectrum recorded for an intermediate mass range of cationic platinum clusters during reaction with methane. The binary reactivity pattern (on–off) is clearly recognized. Partial pressure of methane was 2×10^{-8} mbar, and reaction time was 3 s.

translationally cold. Our estimates based on the voltage settings of the cell, suggest that clusters with $n > 4$ have negligible translational energy. A minor contribution to the over-all energy (typically less than 30 kJ mol^{-1}) should, however, be accounted for in the case of $2 < n \leqslant 4$. The monomer was cooled by pulsed argon.

The extremely poor reactivity of Pt$_n^+$ for n = 4, 10 and 15 parallels the behaviour found by Beyer *et al.* for the reaction with N$_2$O.[6] Fig. 2 shows that the anionic and cationic reactivity towards
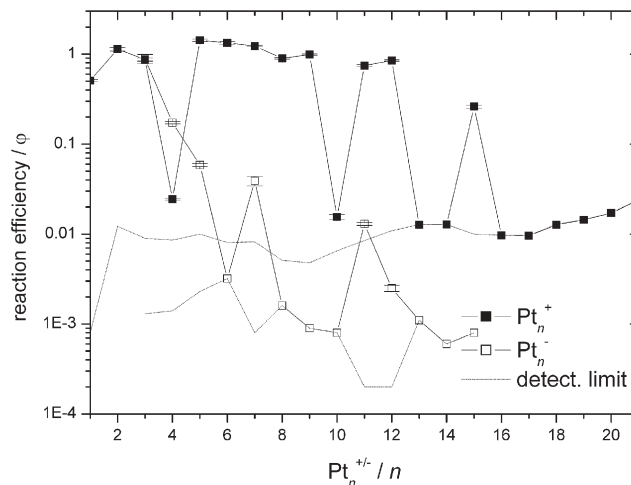

Fig. 2 Size dependent reaction efficiency.

methane are quite different. However, the gross features of Pt_n^- reactivity towards CH_4 and N_2O^6 are the same, although we note that in general methane reacts somewhat slower. As mentioned above, there already exists a study on the reactivity of neutral platinum clusters towards methane up to $n = 24$.[5] In that study, the conditions were significantly different from the present study (much higher pressure, much shorter reaction time). In addition, ion-induced dipole forces affect absolute rates for charged clusters. Despite these differences, we are highly satisfied in noticing that the line describing the relative neutral cluster reactivity–size relationship falls nicely in-between the corresponding cationic and anionic lines (not illustrated here). In particular, the magic number $n = 10$ represents the minimum in reactivity, and reactivity is in general low or very low for $n \geqslant 14$, but increasing slowly with increasing n.

We will be careful in speculating on how the reactivity of the different clusters relates to their thermochemical stability and molecular and electronic structures, since energy differences in the range 10–20 kJ mol^{-1} may account for the observed differences. Despite these considerations, it is clear that in the likely case that CH_2 binds in the form of methylene, platinum must accommodate orbitals of fitting symmetry and energy to form a strong $Pt=C$ double bond (in the case methylene binds to one single platinum atom). Armentrout *et al.* have suggested that in the case of Pt^+, promotion to the low lying $6s^1d^8$ electronic configuration is necessary.[7] It should be mentioned that quantum chemical studies indicate that while platinum clusters typically have layered structures, the unreactive 10-atom Pt cluster has a tetrahedral structure and is relatively more stable than the other clusters.[8] The reaction enthalpy for the reaction, $CH_4 \rightarrow CH_2 + H_2$ is 461.3 kJ mol^{-1} (NIST), and must be compensated by binding the CH_2 unit by at least the same amount, a severe requirement. This fine balance is nicely illustrated by Schwarz and co-workers who observed that the reaction of the tetramer is essentially reversible.

$$Pt_4CH_2^+ + H_2 \rightarrow Pt_4^+ + CH_4 \qquad (3)$$
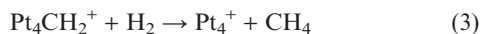
They concluded from the rates of the reverse reaction, that the reaction is almost thermoneutral for $n = 4$ and that the low reactivity in the case of Pt_4^+ was due to a lack of thermodynamic driving force.[2] The same applies to Pt^+, for which DFT calculations from Armentrout's lab demonstrate that there is hardly any barrier for the almost thermoneutral transformation, which is in agreement with their own guided beam measurements.[7]

In order to probe this matter even further, we did experiments where both methane and D_2 were allowed into the cell simultaneously. Fig. 3 illustrates a typical situation. Neither of the reactant or product clusters with $n \leqslant 4$, were very susceptible to the presence of D_2. However, for $n \geqslant 5$ efficient hydrogen–deuterium exchange is observed. This coincides with our own observation for the reaction of Pt_n^+ clusters with molecular hydrogen, where efficient physisorption or chemisorption under FT-ICR conditions is only observed for $n \geqslant 5$.[9]

A characteristic number of hydrogen–deuterium exchanges can serve as a probe for particular structures of gaseous metal hydrocarbon clusters, such as the fivefold exchange of a rhodium allyl hydride,[10] or the four fold exchange for Rh,C_2,H_4^+.[11] Along these lines, we interpret the twofold hydrogen–deuterium exchanges with an intact CH_2 unit which is bound to either one
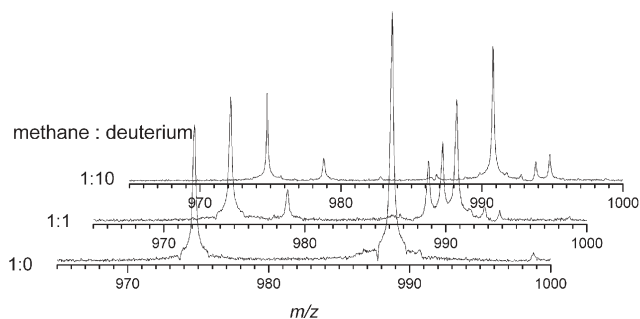

Fig. 3 The portion of the mass spectrum, which displays Pt_5^+ ($m/z = 975$), $Pt_5CH_2^+$ ($m/z = 989$) and deuterium exchange products.

or two platinum atoms. This interpretation is also consistent with the observed reversibility of H_2 loss for Pt_4^+.[2] The hydrogen–deuterium exchange must also be associative, since we were not able to observe any exchange for $n = 1$–4, for which the clusters do not appear to adsorb molecular hydrogen under FT-ICR conditions.

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