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# Activation of methane and methane-$d_4$ by ionic platinum clusters

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## Abstract

Bimolecular reactions of cationic platinum clusters $Pt_n^+$, $n = 1$–24, and anionic platinum clusters $Pt_n^-$, $n = 3$–22, with $CH_4$ and $CD_4$ are studied under low pressure conditions in an FT-ICR mass spectrometer, using an isotopically enriched $^{195}Pt$ sample. Strongly size-dependent dehydrogenation and formation of $Pt_nCH_2^{+/-}$ is observed for both charge states. Starting with $n = 12$, cationic clusters also afford stabilization of a $[Pt_n, CH_4]^+$ adduct, presumably the $HPt_nCH_3^+$ insertion compound. Deuteration shifts the lower limit for adduct formation to $n = 8$. It is suggested that the strong reactivity fluctuations over a wide size range are the gas phase fingerprint of a good heterogeneous catalyst material.
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## 1. Introduction

Reactions of gas phase transition metal ions [1] and ionic clusters with small molecules were intensively studied in the last decades because they can be viewed as the ultimate single-site catalysts [2]. Among the technological applications of platinum in heterogeneous catalysis are hydrogenation reactions [3,4] and the removal of $NO_x$ species from automotive exhaust [5]. In the gas phase, full catalytic cycles have been observed for the oxidation of $H_2$ with $O_2$ on neutral platinum clusters [6] as well as CO with $N_2O$ catalyzed by $Pt^+$ and platinum clusters [7–9], and calculations have shown that relativistic effects are crucial for platinum chemistry [10–12]. Coupling of methane and ammonia [13] and the oxidation of methane [14,15] on $Pt^+$ have been investigated in detail, as well as the reactivity of bimetallic platinum-coinage metal clusters [16–19]. Dehydrogenation of benzene and hexanes by neutral platinum clusters was studied by Trevor et al. [20], and several simple hydrocarbons have been dehydrogenated on small

cationic platinum clusters by Hanmura et al. [21] and Jackson et al. [22].

While activation of methane by $Pt^+$ is after a series of experimental and theoretical studies thoroughly understood [11,14,23–25], the knowledge on the reactivity with platinum clusters remains largely phenomenological [26–29]. Trevor et al. investigated dehydrogenation of methane on neutral platinum clusters with up to 24 atoms in a flow reactor and found that the dehydrogenation degree decreases with cluster size [26]. We have previously studied methane activation by gas phase $Pt_n^{+/-}$ cluster ions with natural isotope distribution for small species with up to nine platinum atoms [27]. Dehydrogenation of methane and formation of platinum cluster carbenes were observed, with a pronounced anomaly for the platinum tetramer: in positive charge state, it was found to be the least reactive species, while in negative charge state, it was the reactivity maximum. A similar observation was later made in reactions with $N_2O$ [30]. The natural platinum distribution, with six stable isotopes made the mass spectra very complicated, therefore it was not possible to conclusively rule out a small contribution of carbide formation or adsorption of $CH_4$ on the cluster. By mass selection of a single mass peak of the isotopomer distribution, Koszinowski et al. later confirmed the exclusive formation of carbenes for cationic clusters with up to five atoms [29], and found evidence that thermochemistry is responsible for the low reactivity of $Pt_4^+$.

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In the present work, highly isotopically enriched platinum $^{195}Pt$ was used to investigate the reactions of $^{195}Pt_n^{+/-}$ clusters, $n = 1$–$24$, with methane $CH_4$ and deuterated methane $CD_4$.

## 2. Experimental details

Isotopically enriched platinum (97.28% $^{195}Pt$, Oak Ridge National Laboratories) was used to investigate the reactions of platinum clusters $^{195}Pt_n^{+/-}$, $n = 1$–$24$ with methane $CH_4$ and deuterated methane $CD_4$ under binary collision conditions in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. The experimental set-up was described in details previously [31]. The platinum ions are produced by pulsed laser vaporisation [32–34] of a rotating platinum disk. The hot metal plasma produced by the laser, which contains enough ions without need for post-ionization, is cooled down and clustered by supersonic expansion of the high pressure gas into high vacuum. Ionic clusters are accelerated along the magnetic field axis by a series of electrostatic lenses, trapped and stored inside the ICR cell in the ultrahigh vacuum of the FT-ICR mass spectrometer. To study the bimolecular cluster ion–molecule reactions the pressure in the ICR cell was raised from the base value of $1 \times 10^{-10}$ mbar to the constant pressure of $2.2 \times 10^{-8}$ mbar by controlled admission of the reactant gas $CH_4$ or $CD_4$ at room temperature. For pressure calibration purposes, it was assumed that the polarizability of $CD_4$ is equal to that of $CH_4$. Commercially available methane $CH_4$ (Messer-Griesheim 99.9%) and deuterated methane $CD_4$ (Cambridge Isotope Laboratories 99%) were used without further purification. For each mass spectrum, clusters generated in 20 laser shots over a period of 2 s were accumulated in the cell. Mass spectra were taken after different reaction delays, and absolute rate constants were extracted assuming pseudo-first order reaction kinetics. Because at nominal $t = 0$, there are different groups of clusters which have experienced different pre-reaction delays, the starting intensities of the product species are treated as variable parameters in the fit. Theoretical collision rates are calculated with the surface charge capture model, which accounts for the finite size and polarizability of the cluster by assuming that a point charge is drawn to the cluster surface due to the interaction with the approaching reactant molecule [35].

## 3. Results

Platinum clusters $Pt_n^{+/-}$, $n = 1$–$24$, react with $CH_4$ and $CD_4$ without change of the number of platinum atoms in the cluster. Thus the reactions for all cluster sizes have been studied under exactly the same conditions, without mass selection. The reactivity of both positively and negatively charged platinum clusters towards $CH_4$ and $CD_4$ was investigated as a function of cluster size.

### 3.1. Reactions of cationic clusters

A typical mass spectrum taken after 2 s reaction delay for the reaction of cationic platinum clusters $Pt_n^+$ with $CH_4$ is presented in Fig. 1, showing a part of the mass spectrum which contains clusters with 4–11 atoms. At the first sight one can observe that their reactivity depends strongly on the cluster size not only with respect to their rate constant, but also to the number of reaction steps they undergo. The first species displayed in Fig. 1, $Pt_4^+$ shows a very low reactivity towards $CH_4$, after 2 s reaction delay only few product is visible in the spectrum. Clusters in the range of $5 \leq n \leq 9$ display an appreciable reactivity.
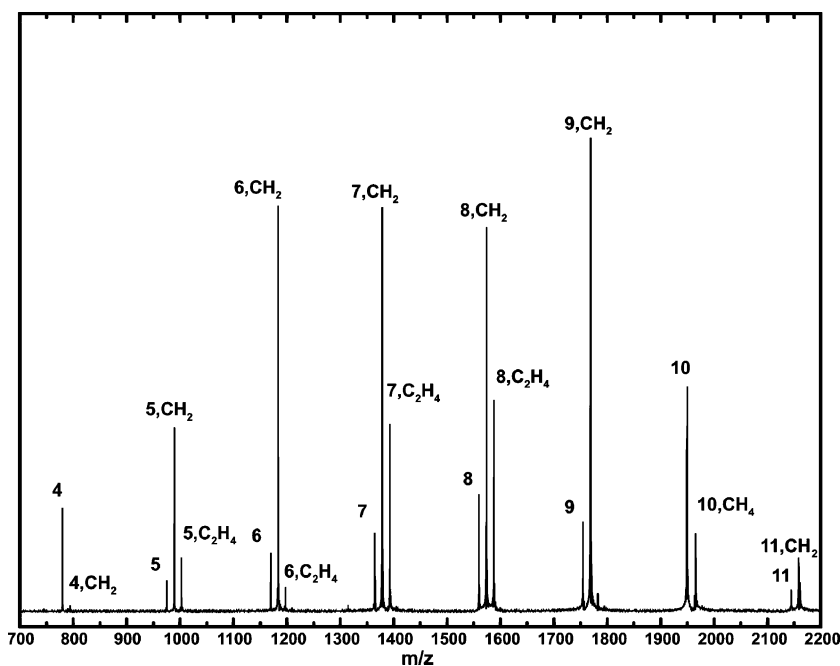


Fig. 1. Mass spectrum of the reaction of cationic platinum clusters $Pt_n^+$, $n = 4$–$11$, with $CH_4$ after 2 s reaction delay, using the isotopically enriched target. Peaks are labelled with their cluster size and primary reaction products, addition of $CH_2$, $CH_4$ or for some species secondary $C_2H_4$. The clusters show a quite irregular reactivity pattern, not only with respect to their rate constant, but also to the number of reaction steps they undergo.
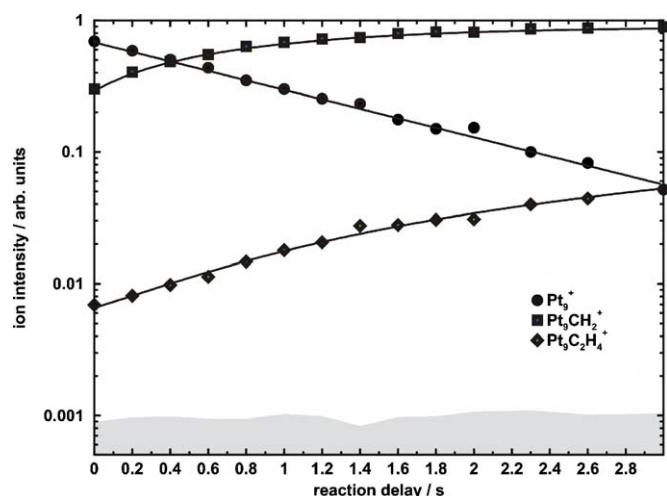
Fig. 2. Kinetic fit for the reaction of $Pt_9^+$ with $CH_4$. The first reaction step, addition of $CH_2$, proceeds efficiently while the secondary $CH_2$ is significantly more slowly attached. Grey shaded area denotes the noise level. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)



Fig. 3. Mass spectrum of the reaction of cationic platinum clusters $Pt_n^+$, $n = 9$–12, with $CD_4$ after 2 s reaction delay. The clusters show, besides dehydrogenation, a second primary product, $Pt_nCD_4^+$.

For all these species the reaction consists in simple dehydrogenation of the methane on the cluster surface. The reaction takes place in sequential steps, a second reaction product being already observed for most of the species, as described by the equations:

$$Pt_n^+ + CH_4 \rightarrow Pt_nCH_2^+ + H_2 \tag{1}$$

$$Pt_nCH_2^+ + CH_4 \rightarrow Pt_nC_2H_4^+ + H_2 \tag{2}$$
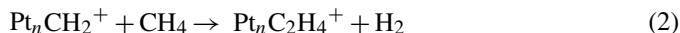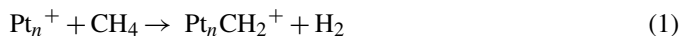
Clusters $n = 6$ and 9 react an order of magnitude more slowly in the secondary step than $n = 5$, 7 and 8.

Quite particular is the behaviour of $Pt_{10}^+$, which is the first species, which adsorbs a complete $CH_4$, without hydrogen elimination. The reaction, however, does not follow first-order kinetics. A small fraction of the clusters rapidly react to the products, while the majority of $Pt_{10}^+$ seems to be unreactive against $CH_4$. This behavior seems quite typical for the larger clusters, it was also observed for $n = 11$ and 13–21, while $n = 12$ and 24 adsorb $CH_4$ following pseudo-first order kinetics:

$$Pt_n^+ + CH_4 \rightarrow Pt_nCH_4^+ \tag{3}$$

Efficient dehydrogenation of $CH_4$ was for the larger clusters only observed for $n = 11$, 12 and 15, while only traces of the $Pt_nCH_2^+$ reaction products were present for $n = 10$, 14 and 17. For $n = 13$, 16 and 18–24, no evidence for methane dehydrogenation was found in the mass spectra.

Rate constants were extracted from a series of mass spectra measured after 14 different reaction delays ranging from the nominal time $t = 0$–3 s. Relative intensities of the reactant and product ions and the corresponding fit are exemplified in Fig. 2 for $Pt_9^+$. The parent ion decay is linear in the semi-logarithmic scale, confirming the absence of platinum cluster fragmentation. The first reaction step, addition of $CH_2$ with elimination of molecular $H_2$ proceeds efficiently, while the rate constant for the secondary $CH_2$ formation is almost 40 times smaller.
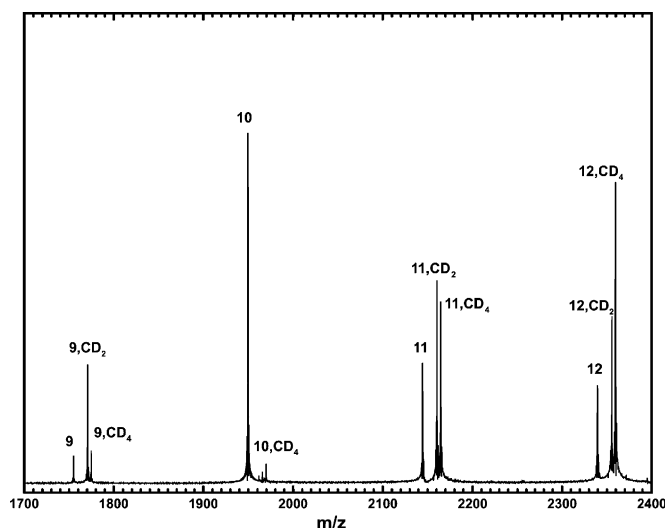
Using deuterated methane $CD_4$ as reactant gas, considerably different results were obtained for certain cluster sizes. While $Pt_n^+$, $n = 1$–3 and 5–7, react with comparable rate constants for both $CH_4$ and $CD_4$, the tetramer is almost unreactive with deuterated methane. $Pt_nCD_4^+$ product species are already observed for $n = 8$ and 9, and the branching ratio between $Pt_nCD_4^+$ and $Pt_nCD_2^+$ is increased for $n = 11$, 12 and 15. Fig. 3 displays a typical mass spectrum taken after 2 s reaction delay for a cluster distribution from $n = 9$ to 12 reacting with $CD_4$. The $n = 9$ species exhibits $CD_2$ as well as $CD_4$ addition, while $Pt_9CH_2^+$ was the only primary product with $CH_4$. The time intensity profile is again exemplified for $Pt_9^+$ in Fig. 4:

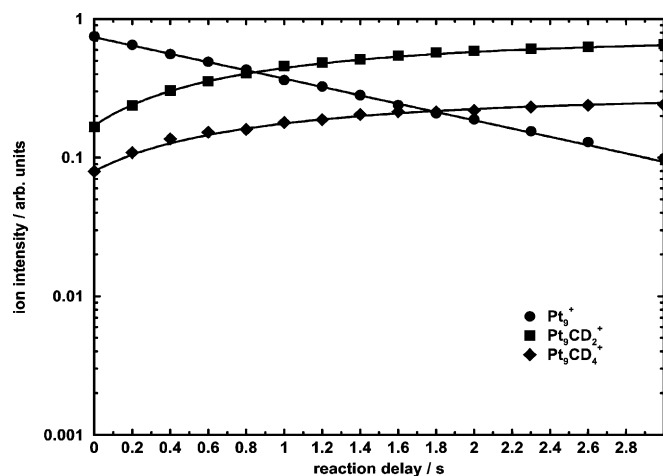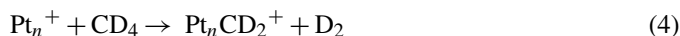$$Pt_n^+ + CD_4 \rightarrow Pt_nCD_2^+ + D_2 \tag{4}$$

$$Pt_n^+ + CD_4 \rightarrow Pt_nCD_4^+ \tag{5}$$



Fig. 4. Kinetic fit for the reaction of $Pt_9^+$ with $CD_4$. $Pt_9^+$ reacts to the primary reaction products $Pt_9CD_2^+$ and $Pt_9CD_4^+$. The secondary product $Pt_9C_2D_4^+$ is barely visible after 3 s and could not be included in the analysis. The noise level lies below 0.001.
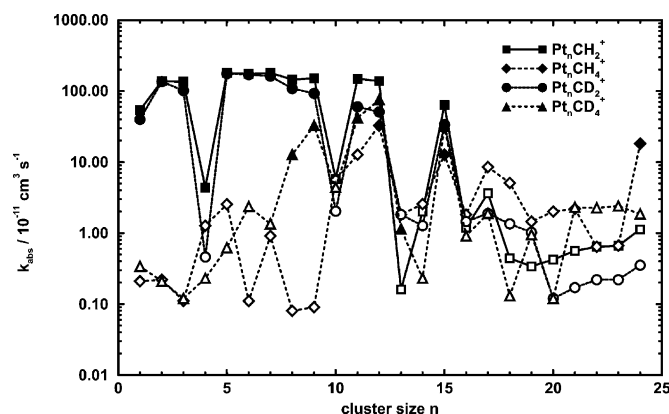
Fig. 5. Absolute rate constants of the first reaction step of $Pt_n^+$ clusters with $CH_4$ and $CD_4$ on a semi-logarithmic scale. Open symbols denote upper limits of the rate constants.

Secondary reactions have been observed for the same cluster sizes as for $CH_4$, equivalent to reaction (3). Similar kinetic evaluation of the reactions were undertaken for all the cationic clusters, $1 \leq n \leq 24$, relative rate constants for the first reaction step for both reactions with $CH_4$ and $CD_4$ were extracted from the kinetic fits and further converted into absolute rate constants, displayed in Fig. 5 and summarized in Table 1, together with collision rates calculated from the surface charge capture model [35]. The most reactive clusters react close to collision rate. However, the surface charge capture model still significantly underestimates the collision rate of ionic platinum clusters with CO [35], so actual reaction efficiencies are most likely between

50 and 100% for the most reactive cluster sizes $n = 5$–9. The differences between the two isotopomers are moderate, but significant. The reactivity of platinum clusters towards $CH_4$ for the dehydrogenation reaction is slightly stronger. For cationic species $n = 8$ and 9 atoms two primary reaction products corresponding to $Pt_nCD_2^+$ and $Pt_nCD_4^+$ were observed while the same cluster sizes reacting with $CH_4$ showed only one reaction product, simple dehydrogenation of the methane. A drastic change in reactivity can be observed for $Pt_{24}^+$, which reacts well with $CH_4$, but no reaction was observed with $CD_4$. The open symbols in Fig. 5 denote upper limits determined from the parent ion intensities and the noise level after the longest reaction delay.

### 3.2. Reactions of anionic clusters

The anionic platinum clusters $Pt_n^-$, $n = 3$–22, were investigated under similar conditions. Monomer and dimer platinum anions are not produced in sufficient quantities in our ion source to allow reactivity studies. Absolute rate constants for the first reaction step were extracted in the same way as for cationic species, and the results are summarized in Fig. 6 and Table 2. The anions behave differently from the cations, they exhibit an overall much slower reactivity towards both reactant gases, $CH_4$ and $CD_4$, with the most reactive size $n = 4$ reaching only 15% of the surface charge capture rate. The only reaction observed is simple dehydrogenation:
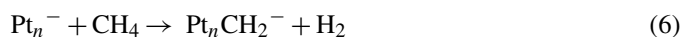
$$Pt_n^- + CH_4 \rightarrow Pt_nCH_2^- + H_2 \tag{6}$$

Table 1
Absolute rate constants $k_{abs}$ for the first reactions' step of cationic platinum clusters, compared to the theoretical collision rate $k_{SCC}$ for platinum clusters with $CH_4$ according to the surface charge capture model [35]

| Cluster | $k_{abs}$ ($\times 10^{-11}$ cm$^3$ s$^{-1}$) | | | | $k_{SCC}$ ($\times 10^{-11}$ cm$^3$ s$^{-1}$) |
|---|---|---|---|---|---|
| | $Pt_nCH_2^{+a}$ | $Pt_nCH_4^{+a}$ | $Pt_nCD_2^{+a}$ | $Pt_nCD_4^{+a}$ | $Pt_n^+ + CH_4^b$ |
| $Pt_1^+$ | 53.5 | <0.21 | 39.9 | <0.34 | 145 |
| $Pt_2^+$ | 138 | <0.22 | 135 | <0.21 | 156 |
| $Pt_3^+$ | 134 | <0.11 | 102 | <0.12 | 165 |
| $Pt_4^+$ | 4.35 | <1.27 | <0.46 | <0.23 | 172 |
| $Pt_5^+$ | 180 | <2.56 | 176 | <0.62 | 179 |
| $Pt_6^+$ | 174 | <0.11 | 171 | <2.36 | 184 |
| $Pt_7^+$ | 180 | <0.91 | 161 | <1.34 | 190 |
| $Pt_8^+$ | 145 | <0.08 | 108 | 12.7 | 195 |
| $Pt_9^+$ | 151 | <0.09 | 92.5 | 32.7 | 200 |
| $Pt_{10}^+$ | <5.81 | <5.62 | <2.03 | <4.39 | 204 |
| $Pt_{11}^+$ | 149 | <12.7 | 59.9 | 41.7 | 209 |
| $Pt_{12}^+$ | 138 | 32.7 | 50.8 | 74.9 | 213 |
| $Pt_{13}^+$ | <0.16 | <1.81 | <1.81 | 1.14 | 217 |
| $Pt_{14}^+$ | <2.01 | <2.56 | <1.27 | <0.23 | 220 |
| $Pt_{15}^+$ | 63.5 | <12.7 | 33.6 | 31.8 | 224 |
| $Pt_{16}^+$ | <1.18 | <1.81 | <1.45 | <0.91 | 227 |
| $Pt_{17}^+$ | <3.64 | <8.53 | <1.87 | <1.88 | 230 |
| $Pt_{18}^+$ | <0.44 | <5.08 | <1.34 | <0.13 | 234 |
| $Pt_{19}^+$ | <0.34 | <1.45 | <1.02 | <0.95 | 237 |
| $Pt_{20}^+$ | <0.42 | <2.00 | <0.12 | <0.12 | 240 |
| $Pt_{21}^+$ | <0.56 | <2.18 | <0.17 | <2.30 | 243 |
| $Pt_{22}^+$ | <0.64 | <0.64 | <0.22 | <2.26 | 245 |
| $Pt_{23}^+$ | <0.66 | <0.66 | <0.22 | <2.40 | 248 |
| $Pt_{24}^+$ | <1.13 | 18.1 | <0.35 | <1.85 | 251 |

[a] Reaction products.
[b] Calculated collision rate.
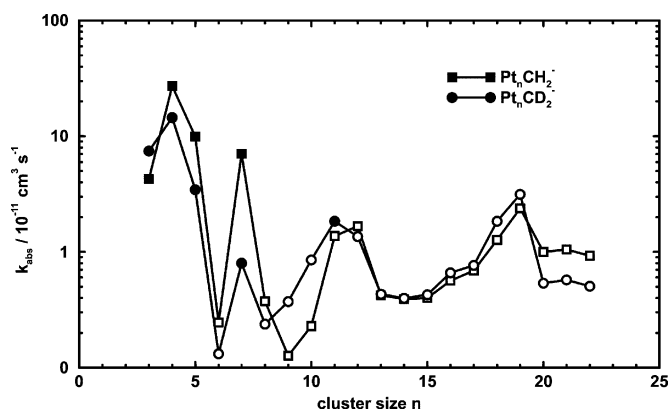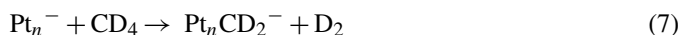
Fig. 6. Absolute rate constants of the first reaction step of $Pt_n^-$ clusters with $CH_4$ and $CD_4$ on a semi-logarithmic scale. Open symbols denote upper limits of the rate constants. Monomer and dimer platinum anions are not produced in sufficient quantities.

$$Pt_n^- + CD_4 \rightarrow Pt_nCD_2^- + D_2 \tag{7}$$

Overall there are not significant differences between the reactions of the anions with methane and deuterated methane. They follow almost the same size-dependence in reactivity, however, with the exception of $n = 3$ and 11, the reactivity of the anions towards $CD_4$ is slightly smaller than $CH_4$. As previously reported [27], the most reactive anion studied is $Pt_4^-$, while the cation $Pt_4^+$ exhibits a deep reactivity minimum. The anion $n = 6$ is almost unreactive, while the corresponding cationic species shows a quite strong reactivity towards both reactants. Starting with $n = 12$ the anions are almost unreactive, and upper limits for their rate constants are given.

Table 2

Absolute rate constants for the first reaction step of anionic platinum clusters, compared to the theoretical collision rate $k_{SCC}$ for platinum clusters with $CH_4$ according to the surface charge capture model [35]

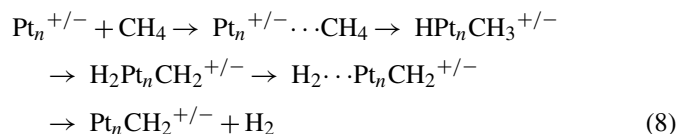| Cluster | $k_{abs}$ ($\times 10^{-11}$ cm$^3$ s$^{-1}$) | | $k_{SCC}$ ($\times 10^{-11}$ cm$^3$ s$^{-1}$) |
| --- | --- | --- | --- |
| | $Pt_nCH_2^{-a}$ | $Pt_nCD_2^{-a}$ | $Pt_n^- + CH_4^b$ |
| $Pt_3^-$ | 4.26 | 7.43 | 165 |
| $Pt_4^-$ | 27.2 | 14.5 | 172 |
| $Pt_5^-$ | 9.97 | 3.44 | 179 |
| $Pt_6^-$ | <0.24 | <0.13 | 184 |
| $Pt_7^-$ | 7.07 | 0.79 | 190 |
| $Pt_8^-$ | <0.37 | <0.23 | 195 |
| $Pt_9^-$ | <0.12 | <0.37 | 200 |
| $Pt_{10}^-$ | <0.22 | <0.85 | 204 |
| $Pt_{11}^-$ | <1.37 | <1.83 | 209 |
| $Pt_{12}^-$ | <1.66 | <1.35 | 213 |
| $Pt_{13}^-$ | <0.42 | <0.43 | 217 |
| $Pt_{14}^-$ | <0.39 | <0.39 | 220 |
| $Pt_{15}^-$ | <0.39 | <0.42 | 224 |
| $Pt_{16}^-$ | <0.56 | <0.65 | 227 |
| $Pt_{17}^-$ | <0.68 | <0.76 | 230 |
| $Pt_{18}^-$ | <1.27 | <1.83 | 234 |
| $Pt_{19}^-$ | <2.37 | <3.13 | 237 |
| $Pt_{20}^-$ | <0.99 | <0.53 | 240 |
| $Pt_{21}^-$ | <1.05 | <0.57 | 243 |
| $Pt_{22}^-$ | <0.92 | <0.50 | 245 |

[a] Reaction products.
[b] Calculated collision rate.

## 4. Discussion

Interestingly, some features in the size-dependence of the neutral clusters [26] have their counterpart in the reactivity of anionic species, while others have parallel behaviour in the cationic ones. The local reactivity maximum at $n = 7$ is observed only with anions, while cations show uniformly high reactivities from $n = 5$–9. The local reactivity maxima at $n = 11$, 12 and 15 are, on the other hand, observed only with cations. The overall decrease of reactivity with cluster size, however, is a common feature of the three charge states. For the cations, the same reactivity maxima and minima, with the exception of $n = 24$, have been observed in the reaction of platinum clusters with $N_2O$ [30]. Koszinowski et al. have shown that the reactivity minimum for $Pt_4^+$ with $CH_4$ is due to the thermochemistry of reaction (1) for this specific cluster size [29]. Whether the origin of the other size effects is of electronic, geometric or again thermochemical nature cannot be decided at this point. However, as outlined previously, e.g. for silver clusters [36,37], electronic and geometric structure are intimately related, and together determine thermochemical properties and chemical reactivity.

Quantum chemical calculations have shown that the dehydrogenation of the methane on $Pt^+$ proceeds via a hydride–methyl insertion complex, which represents the global minimum on the potential energy surface [14,23,25]. As discussed previously [27,28], this well-established potential energy surface can also explain the reactivity of the cluster species. When a $CH_4$ molecule collides with a platinum cluster, an electrostatically bound complex is presumably formed, $Pt_nCH_4^{+/-}$. This step is followed by the insertion of a platinum atom into one of the C–H bonds of methane, resulting into a hydride–methyl platinum structure, $HPt_nCH_3^{+/-}$. In the next step along the reaction path, a second hydrogen atom migrates from the methyl radical to the platinum cluster. Further rearrangements, driven by the internal energy of the hot cluster, may lead to formation of a dihydrogen complex of the platinum carbene, $H_2Pt_nCH_2^{+/-}$. Dehydrogenation of the methane becomes evident when a hydrogen molecule $H_2$ is ultimately released from the cluster surface.

$$Pt_n^{+/-} + CH_4 \rightarrow Pt_n^{+/-} \cdots CH_4 \rightarrow HPt_nCH_3^{+/-}$$
$$\rightarrow H_2Pt_nCH_2^{+/-} \rightarrow H_2 \cdots Pt_nCH_2^{+/-}$$
$$\rightarrow Pt_nCH_2^{+/-} + H_2 \tag{8}$$

Larger clusters already have a significant heat capacity, and the lifetime of the intermediate complexes along the potential energy surface increases with cluster size [38]. Radiative stabilization [39,40] is ultimately responsible for the observation of a nominal $CH_4$ adduct for cationic $n = 10$, 12 and 15. $Pt_{24}^+$ exclusively forms this adduct, without dehydrogenation. While no information on the actual structure is available, it seems reasonable to assume that the $Pt_nCH_4^+$ species are radiatively stabilized in the lowest minimum of the potential energy surface, which presumably is an insertion complex of the form $HPt_nCH_3^+$ or $H_2Pt_nCH_2^+$.

The kinetic isotope effect in the reactions with deuterated methane $CD_4$ has no straightforward explanation, which is

quite reasonable, since a number of effects contribute in a strongly non-linear manner: The density of states is higher in complexes with deuterated species, therefore the stabilization of the $CD_4$ adduct is favoured compared to $CH_4$. This argument obviously dominates for $n = 8$, 9, 11, 12, and 15 in the cationic species. However, the stabilization of $Pt_{24}CH_4^+$ may be explained by a subtle thermochemical difference. For $HPtCH_3^+$ versus $DPtCD_3^+$, we have previously calculated that keeping $CD_4$ in the gas phase is more favourable by ∼2.5 kJ/mol compared to $CH_4$, due to the subtle differences in zero-point energy between the free and the adsorbed molecule [25]. If this is the correct explanation, this means that stabilization of $Pt_{24}CH_4^+$ happens in a narrow thermochemical window. It is obviously also strongly dependent on the internal energy of the reactant cluster, which is not known in the present experiment.

## 5. Conclusions

The reactivity of cationic and anionic platinum clusters with up to 24 atoms exhibits strong size-dependence, with an overall decrease in reactivity for clusters with 10 atoms or more. The strong local reactivity maxima and minima observed previously for clusters $n < 10$ are also found for larger cationic clusters, while the reactivity of anionic clusters is weak for $n > 11$, where only upper limits can be given for the rate constants. Only cationic clusters afford the stabilization of a nominal $Pt_nCH_4^+$ adduct, which probably is an insertion product like $HPt_nCH_3^+$ or $H_2Pt_nCH_2^+$. Deuteration shifts the minimum cluster size for this process from $n = 12$ to 8. These findings underline the chemical bandwidth of platinum, for which small changes in the electronic and geometric environment lead to large changes in its reactivity. This is the gas phase fingerprint of a potent catalyst material.

## Acknowledgements

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