Reactivity of Small Cationic Platinum Clusters[†]

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The gas-phase reactions between Pt_n^+ clusters ($n = 1-5$) and the inorganic substrates H_2, O_2, NH_3, H_2O, CO_2, and N_2O have been investigated using FT-ICR mass spectrometry. It is found that Pt_2^+ is unique in efficiently activating NH_3 whereas the other clusters simply add this reactant in the primary reactions. The consecutive products $Pt_4(NH_3)_3^+$ and $Pt_5NH_3^+$, however, also induce dehydrogenation of further NH_3. Reactions of Pt_n^+ with N_2O effect O transfer, those with O_2 lead to degradation of the platinum clusters by loss of neutral PtO_2. Only Pt_5^+ is observed to add H_2 and H_2O with low efficiencies whereas no reactions at all occur with CO_2. In addition, the reactions between Pt_n^+ and CH_4 have been reinvestigated. Besides confirming the results previously reported, evidence is found that thermodynamics accounts for the anomalously low reactivity of Pt_4^+. Comparing the reactivity of Pt_n^+ clusters with that of Pt surfaces shows distinct similarities and, thus, encourages use of the former in the development of gas-phase models for heterogeneous catalysis.

I. Introduction

During the last two decades, studies of metal clusters in the gas phase have been established as a major area within the fields of physical chemistry and molecular physics. The motivation for research on metal clusters mainly is 2-fold. First, clusters lie between the atomic scale and that of the solid state so that they are ideally suited to serve as a probe for the transition between these two forms of matter.[1,2] This is particularly intriguing in the case of metals because the characteristic properties of the metallic state, such as conductivity, ductility, and shininess, inherently depend on the degree of aggregation. Studying the physical and chemical behavior of metal clusters thus promises to improve our understanding of these and other important phenomena related to the formation of condensed matter. Second, metal clusters and especially those of transition metals are used as models for heterogeneous catalysts.[2,3] This approach suggests that the basic chemical features of a given heterogeneous catalyst are mimicked by clusters of the same elemental composition while the size of the system under investigation is simultaneously drastically reduced. Indeed, the enormous complexity of real catalysts is a fundamental obstacle to mechanistic in situ studies and explains why so many catalytic processes escape from thorough elucidation to date.[4]

In contrast, advanced mass spectrometry allows the investigation of the chemical reactivity of size-selected metal clusters in the gas phase and also offers opportunities to refine the model system by adding ligands or solvents in a highly controllable manner. Further, mass spectrometry can provide a sound basis for elaborate theoretical studies, although the latter are far from trivial in the case of transition-metal clusters and their reactions.

One of the most versatile metals in catalytic applications certainly is platinum.[5] Inter alia, platinum catalysts are crucially involved in hydrocracking and platforming in the petrol industry, in dehydrogenation and hydrogenation reactions, in the synthesis of nitric acid, in the Degussa and Andrussov processes

for the large-scale synthesis of hydrogen cyanide, and last but not least in the decomposition of carbon monoxide and nitrous oxide in automotive catalytic converters. Considering the importance of these processes, it comes as no surprise that many of the corresponding reactions have been studied using platinum clusters as model systems. Pioneering work of Kaldor, Cox, and co-workers demonstrated that neutral platinum clusters Pt_n ($n < 25$), like bulk phase platinum, readily chemisorb hydrogen[6] and undergo extensive dehydrogenation reactions with the hydrocarbons methane, benzene, and several isomers of hexane.[3,7,8] Additionally, Kaldor and Cox reported that also positively charged clusters Pt_n^+ activate methane.[3] These reactions have been studied in detail by Bondybey and co-workers who observed dehydrogenation yielding the carbenes $Pt_nCH_2^+$.[9] Interestingly, all clusters studied up to Pt_9^+ react very efficiently, Pt_4^+ being the only exception, whereas the situation is just the opposite for the corresponding anionic Pt_n^- clusters. With respect to small cationic platinum clusters Pt_n^+, Michl and co-workers ($n \leq 2$),[10] the group of Marshall ($n \leq 4$),[11] and, very recently, Hanmura et al. ($n \leq 5$)[12] showed that these species also induce dehydrogenation of ethane, ethylene, acetylene and of larger hydrocarbons such as *n*-butane, cyclohexane, and benzene.

Regarding small anionic clusters Pt_n^- ($n = 3-7$), further reactions have been examined by Ervin and co-workers. Upon reaction with N_2, O_2, CO, and CO_2, these clusters form association products accompanied by various degrees of cluster fragmentation whereas only transfer of oxygen was observed in the reaction with N_2O.[13,14] The resulting clusters Pt_nO^- react with CO, yielding Pt_n^- and CO_2, thus providing an example of complete catalytic cycle in the gas phase.[15,16] In addition, Ervin's group investigated collision-induced dissociations of Pt_n^- and $Pt_n(CO)_x^-$ clusters by means of guided-ion beam mass spectrometry.[17]

Although this manifold of studies has much improved our knowledge of the chemistry of platinum clusters, it does by far not suffice to fully characterize and understand their reactivity. Particularly in the case of cationic clusters, almost exclusively
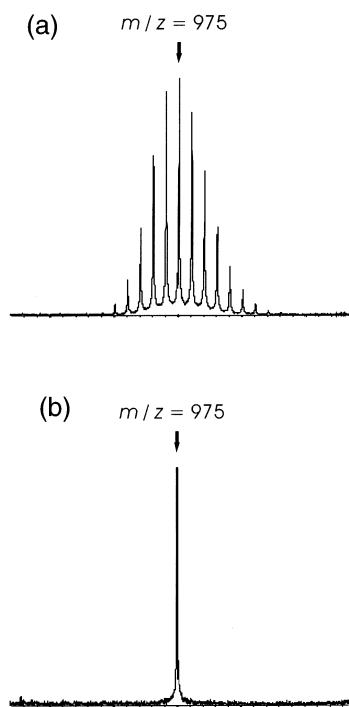
Figure 1. *m/z* range from 962 to 988 (a) prior to and (b) after mass selection and thermalization of $^{195}Pt_5^+$.[27]

reactions with hydrocarbons have been examined so far. For developing further and more complex models of catalytic processes in the gas phase, surely also other substrates have to be applied as reactants. As a first step toward this end, here we report on the reactions of small cationic platinum clusters Pt_n^+ ($n \leq 5$) with H_2, O_2, NH_3, H_2O, CO_2, and N_2O, studied by Fourier-tranform ion-cyclotron resonance (FT-ICR) mass spectrometry; in addition, we have reinvestigated the reactions between Pt_n^+ ($n \leq 5$) and CH_4. Our focus on small clusters is due to the fact that for these a comparison of their reactivity with results gained for atomic Pt^+ in our laboratory is straightforward.[18-21] Moreover, our experimental setup is favorable for the generation of relatively small cluster ions.

II. Experiment

Experiments were performed using a Spectrospin CMS 47X FT-ICR mass spectrometer that has been described in detail before.[22,23] Recently,[24] the instrument has been equipped with a Smalley-type[25] cluster-ion source developed by Bondybey, Niedner-Schatteburg, and co-workers.[26] In brief, the fundamental of a pulsed Nd:YAG laser ($\lambda = 1064$ nm, Spectron Systems) is focused onto a rotating platinum target. The metal plasma thereby generated is entrained in a synchronized helium pulse and cooled by supersonic expansion so that cluster formation can occur. After passing a skimmer, the ionic components of the molecular beam are transferred into the analyzer cell by means of electrostatic potentials and lenses. There, the ions are trapped in the field of a 7.05 T superconducting magnet. The distribution of cluster ions thus produced can be somewhat controlled by varying the delays between helium pulse, laser shot, and inlet into the analyzer cell. However, the best intensities achieved for the clusters are still about an order of magnitude smaller than those of the Pt^+ monomer. For the larger clusters, the situation is even more unfavorable because the intensity is spread over the broad isotopic distribution arising for platinum clusters (Figure 1a). The existence of several

isotopomers can also complicate the analysis of products formed from Pt_n^+ as, e.g., the degree of dehydrogenation may thus be obscured. Whereas Marshall and co-workers handled this problem by application of polynomial methods,[11] we haven chosen a different approach and isolated a single isotopomer for every cluster size, namely the formal $^{195}Pt_n^+$ isotopomer,[27] by using the FERETS technique (Figure 1b).[28] For the larger clusters, the ejection of the neighboring isotopomers (Δ $m/z = 1$) in the isolation procedure inevitably leads to a minor, but undesired kinetic excitation of the $^{195}Pt_n^+$ ions themselves. After mass selection, the ions were therefore always thermalized to ambient temperature by pulsing-in argon. Thermalization was assumed to be complete when the rates for the reactions of the mass-selected clusters did not any more depend on the number of argon pulses applied (typically, a single pulse reaching a pressure of $\geq 10^{-5}$ mbar for about 0.5 s was sufficient). A further probe for eventually kinetically excited clusters is achieved upon reaction with methane. Whereas thermalized Pt_n^+ clusters, $n = 2-5$, solely undergo single dehydrogenation leading to $Pt_nCH_2^+$ (see below), kinetic excitation affords double dehydrogenation, giving Pt_nC^+. In all cases, the kinetic analyses (see below) showed exponential decays that exclude significant contributions of kinetic or electronic excitation as well.

Ion—molecule reactions then were studied by leaking-in the neutral reactant at $p \approx 5 \times 10^{-9}$ to 10^{-6} mbar and recording the decline of the reactant Pt_n^+ clusters and the evolution of corresponding products. Kinetic analyses yielding bimolecular rate constants k were derived on the basis of the pseudo first-order kinetic approximation. The error of the rate constants reported is estimated at $\pm 30\%$[29] in general and $\pm 50\%$ in the cases of NH_3 and H_2O because of their unfavorable pumping characteristics. Consecutive reactions were analyzed using numerical routines.[30,31] Particularly for the larger clusters studied, extensive data accumulation (up to 1000 scans) was necessary for achieving reasonable signal-to-noise ratios.

III. Results and Discussion

At the outset, let us point to some general characteristics of ion—molecule reactions in the highly diluted gas phase important for the present study. Like in the condensed phase, without an external input of energy, at room temperature only exothermic or approximately thermoneutral reactions can take place with measurable rate constants as long as entropic effects do not play a major role. Because the interaction between an ion and a dipole (permanent or charge-induced) always is attractive, there are no thermochemical constraints with respect to the formation of ion—molecule complexes in the first step. The fact that rate constants measured for formation of such complexes in the highly diluted gas phase are often quite small is readily explained by the absence of a heat bath, which could consume the excess energy released during complex formation and thus prevent its dissociation in the back-reaction. In contrast, efficient reactions are observed in many cases if the collision complex can be stabilized by elimination of a fragment carrying away the excess energy.

For the reactions of platinum clusters Pt_n^+ investigated here, the modes in which the initial collision complex is stabilized can be divided into three types.

Mere Association. No atom or molecule is ejected from the initial encounter complex which, instead, is stabilized by IR photon emission[32] and/or collisions with the highly diluted neutral.

Addition/Elimination. The ion—molecule complex stabilizes by eliminating a fragment of the neutral reactant.

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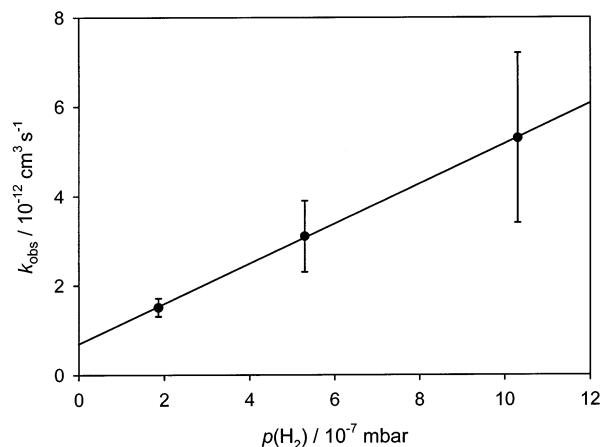
Figure 2. Apparent rate constants for the association reaction between Pt_5^+ and H_2 (reaction 1a) at three different pressures and linear extrapolation to $p = 0$.

**TABLE 1: Apparent Rate Constants k_{obs} and Efficiencies φ for the Association Reactions between Pt_n^+ and H_2, NH_3, H_2O, and CO_2, Respectively**

reaction	n	$k_{obs}/cm^3 s^{-1}$ a	$\varphi = k_{obs}/k_c$ b
$Pt_n^+ + H_2 \rightarrow Pt_nH_2^+$	1–4	$\leq 10^{-13}$	$< 10^{-4}$
	5^c	7.0×10^{-13}	5.0×10^{-4}
$Pt_n^+ + NH_3 \rightarrow Pt_nNH_3^+$	1^d	5.0×10^{-13}	3.0×10^{-4}
	3^e	5.4×10^{-12}	3.0×10^{-3}
	4^f	2.3×10^{-11}	1.2×10^{-2}
	5^g	2.0×10^{-10}	0.1
$Pt_n^+ + H_2O \rightarrow Pt_nH_2O^+$	1–4	$\leq 2.0 \times 10^{-13}$	$< 10^{-4}$
	5^h	1.7×10^{-12}	7.0×10^{-4}
$Pt_n^+ + CO_2 \rightarrow Pt_nCO_2^+$	1–5	$\leq 5.0 \times 10^{-13}$	$< 10^{-3}$

^{a} Errors estimated at ±50%. Only in the case of H_2 has extrapolation to zero pressure been performed; the other rate constants presumably contain contributions of termolecular stabilization. ^{b} Collision rates calculated according to capture theory.[33] ^{c} Bimolecular rate constant, see text. ^{d} Taken from ref 19. ^{e} No significant differences in k_{obs} for $p = 7 \times 10^{-8}$, 3×10^{-7}, and 8×10^{-7} mbar. Average value given for k_{obs}. ^{f} No significant differences in k_{obs} for $p = 8 \times 10^{-8}$, 2×10^{-7}, and 5×10^{-7} mbar. Average value given for k_{obs}. ^{g} No significant differences in k_{obs} for $p = 8 \times 10^{-9}$, 2×10^{-8}, and 5×10^{-8} mbar. Average value given for k_{obs}. ^{h} $p = 3 \times 10^{-7}$ mbar.

Addition/Degradation. The initial collision complex is stabilized by loss of a neutral platinum fragment, referred to as cluster degradation.

Mere Association. As mentioned above, for this type of reaction the only possibilities to release the excess energy of the ion−molecule complex are IR emission and collisional deactivation. The ratio between these two mechanisms is investigated for the reaction of platinum clusters with dihydrogen. Whereas no reactions are observed for Pt_n^+, $n = 1–4$ ($k_{obs} \leq 10^{-13}$ cm^3 s^{-1}, $p(H_2) \approx 10^{-6}$ mbar), association with H_2 takes place in the case of the pentamer

$$Pt_5^+ + H_2 \rightarrow Pt_5H_2^+ \tag{1a}$$
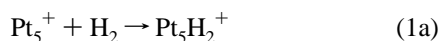
The apparent bimolecular rate constant k_{obs}(1a) determined at different pressures $p(H_2)$ clearly shows a linear dependence, which indicates termolecular stabilization of the adduct (Figure 2). However, extrapolation to $p(H_2) = 0$ gives a positive k value that can be identified with the true bimolecular rate constant. For this, obviously only IR photon emission but no collisional deactivation is operative. Its small value, $k(1a) = (7 \pm 4) \times 10^{-13}$ cm^3 s^{-1}, which corresponds to a reaction efficiency $\varphi \equiv k/k_c \approx 5 \times 10^{-4}$ (Table 1; in this work, collision rates k_c are calculated according to capture theory),[33] implies that most of

SCHEME 1
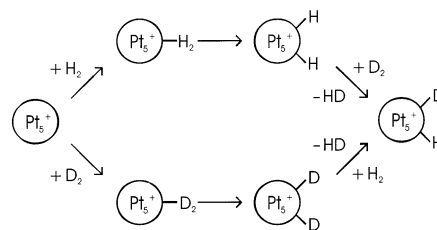
the initially formed collision complexes dissociate before stabilization by IR emission can occur.

$$Pt_5H_2^+ + H_2 \rightarrow Pt_5H_4^+ \tag{1b}$$
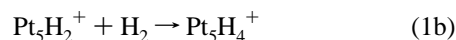
In this context, also a comparison of k(1a) with the rate constant of the secondary reaction 1b, k(1b), is of interest. $Pt_5H_2^+$ reacts approximately twice as efficiently as Pt_5^+, and this difference most probably results from the former's higher number of degrees of freedom. Such an increase in the system's sum of states allows a faster redistribution of internal energy and thus raises the lifetime of the collision complex, thereby also increasing the probability for IR emission or collisional stabilization. Similar effects have been reported for other simple association reactions.[34] The fact that only the largest platinum cluster studied shows a measurable reactivity toward H_2 is accordingly explained in this way.

The rate constant for a third association of H_2 decreases again, which indicates that saturation effects begin to come into play. However, the highest uptake of H_2 observed under FT-ICR conditions, namely formation of $Pt_5H_8^+$, still is much lower than that of the clusters $Pt_nH_{5n}^+$ ($n < 25$) found by Kaldor and Cox under flow-tube conditions.[6] Unfortunately, these authors only briefly mention their findings regarding the reactions between Pt_n^+ clusters and H_2, so that no further comparison is possible.

The reaction of Pt_5^+ with D_2 shows similar ratios between the rate constants for the primary and the secondary association. Because no pressure extrapolation was attempted, only the apparent rate constant can be compared to that of the corresponding reaction with H_2. Taking into account the different collision rates for H_2 and D_2, a kinetic isotope effect of 1.2 ± 0.3 is obtained for $p \approx 10^{-6}$ mbar. Interestingly, exposure of Pt_5^+ to a mixture of H_2 and D_2 gives rise to $Pt_5H_2^+$, Pt_5HD^+, $Pt_5D_2^+$, and higher adducts. The occurrence of isotopic scrambling is clear evidence for dissociative chemisorption of H_2 (and D_2) on Pt_5^+, leading from the initial collision complexes to dihydrido complexes (Scheme 1).

$$Pt_n^+ + yNH_3 \rightarrow Pt_nNH_3^+ + (y-1)NH_3 \rightarrow \rightarrow Pt_nN_yH_{3y}^+ \tag{2}$$
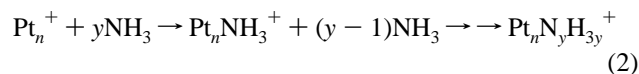
Association products also were observed when reacting Pt_n^+ clusters with ammonia, reaction 2; a remarkable exception being the platinum dimer whose anomalous reactivity is described below. For the Pt^+ monomer, addition of one NH_3 ligand is so slow under FT-ICR conditions ($k_{obs} \approx 5 \times 10^{-13}$ cm^3 s^{-1}) that the product is hardly detectable, although it has a considerable binding energy, $D_0(Pt^+-NH_3) = 310$ kJ mol^{-1}, according to DFT calculations.[19] Again, this behavior can be rationalized by the lack of efficient ways to release the excess energy of the collision complex. Enlarging the system by addition of Pt atoms and NH_3 ligands causes significant rate acceleration due to the increased lifetimes of the collision complexes. Pt_5^+, for example, shows an adsorption rate corresponding to $\varphi \approx 0.1$ (Table 1). As for H_2, the radiative portion of the observed rate constants
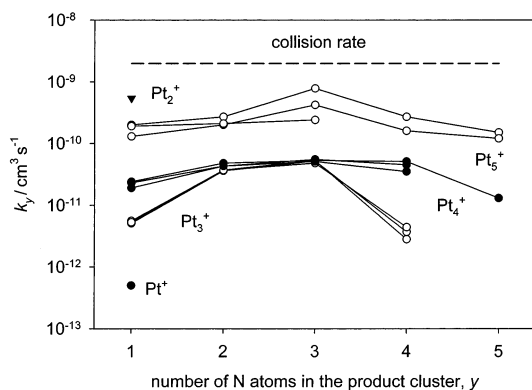
Figure 3. Rate constants k_y of the sequential reactions between Pt_n^+ and NH_3. The kinetic model only accounts for consecutive reactions according to $Pt_nN_{y-1}H_{3(y-1)}^+ + NH_3 \rightarrow Pt_nN_yH_{3y-2x}^+ + xH_2$. Particularly, it does not distinguish between reactions 2 ($x = 0$) and 3 ($x = 1$) for a given number of N atoms in the product, i.e., y, but shows the overall effective rate constants. For several reactions, the data of three experiments performed at different pressures are shown. In the case of Pt_2^+, the rate constant given corresponds to dehydrogenation in the primary reaction 8a (see below).

might be derived by extrapolation to $p = 0$. For NH_3, however, this method is less practical because the pressure dependence of the association rates appears to be significantly weaker and also the data quality is poorer because of the difficulties in maintaining a constant pressure $p(NH_3)$ during the experiments. Therefore, the rate constants provided for reaction 2 are, strictly speaking, only apparent constants containing termolecular contributions.

For a given cluster size, the association rates pass through a maximum and decrease for higher degrees of ligation (Figure 3), thus indicating saturation effects as for the reactions between Pt_5^+ and H_2. Whereas the trimer Pt_3^+ was observed to add up to four NH_3 molecules according to reaction 2, the tetramer and particularly the pentamer not only undergo such simple association reactions but also lose dihydrogen once a certain degree of ligation has been reached, reaction 3.

$$Pt_nN_yH_{3y}^+ + NH_3 \rightarrow Pt_nN_{y+1}H_{3y+1}^+ + H_2 \qquad (3)$$
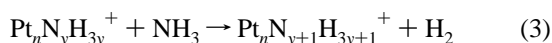
In the case of Pt_4^+, the cluster has to add three NH_3 ligands before reaction 3 occurs with a fourth molecule (together with simple association according to reaction 2). For Pt_5^+, this type of reactivity is already observed in the reaction with the second NH_3 molecule, and it becomes the dominating product channel for $y = 2$.[35] Whereas the loss of H_2 inherently implies activation of NH_3 by the platinum cluster, it cannot be judged a priori if also in the $Pt_nN_yH_{3y}^+$ species platinum has inserted into an N–H bond. To further investigate this question, Pt_5^+ was exposed to a mixture of NH_3 and D_2. In the resulting products, H/D scrambling occurred only for clusters containing three or more nitrogen atoms, consistent with loss of H_2 predominating from this degree of association on. Hence, no indication of dissociative chemisorption is found for either $Pt_5NH_3^+$ or $Pt_5N_2H_6^+$, so that rather these are assumed to contain intact NH_3 molecules.
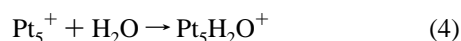
$$Pt_5^+ + H_2O \rightarrow Pt_5H_2O^+ \qquad (4)$$

In the reactions of Pt_n^+ with water, only the pentamer reacts under formation of the corresponding adduct $Pt_5H_2O^+$, reaction 4, at a measurable rate ($k_{obs} = 1.7 \times 10^{-12}$ cm^3 s^{-1}, corresponding to $\varphi = 7 \times 10^{-4}$, $p(H_2O) = 3 \times 10^{-7}$ mbar). For the smaller clusters, an upper limit for their rate constants of $k <$

2×10^{-13} cm^3 s^{-1} was found. Compared with ammonia, the reduced reactivity of water toward cationic platinum clusters can be attributed to its lower basicity because the resulting shallower potential well of the collision complex (DFT predicts $D_0(Pt^+-H_2O) = 180$ kJ mol^{-1} vs $D_0(Pt^+-NH_3) = 310$ kJ mol^{-1})[19,36] is supposed to be associated with a decrease in lifetime. The lower number of degrees of freedom for water, compared to ammonia, presumably enhances this effect.

$$Pt_n^+ + CO_2 \rightarrow Pt_{n-1}^+ + [Pt,C,O_2] \qquad (5)$$
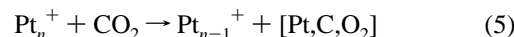
Finally, in the reactions of Pt_n^+ with carbon dioxide, association products could not be detected even for the pentamer. However, for Pt_4^+ und Pt_5^+, degradation according to reaction 5 cannot be excluded rigorously, as this type of reactivity might be obscured by the inevitable presence of traces of O_2, readily yielding the same ionic products (see below). Nevertheless, upper limits for the efficiency of reaction 5 can be derived as $\varphi \leq 5 \times 10^{-4}$ and $\leq 5 \times 10^{-3}$ for the tetramer and pentamer, respectively.

Addition/Elimination. The prototype of this reaction in the case of platinum clusters is dehydrogenation of methane according to

$$Pt_n^+ + CH_4 \rightarrow Pt_nCH_2^+ + H_2 \qquad (6a)$$
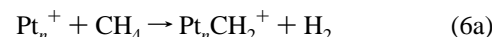
In the case of the monomer, the potential-energy surface of the Pt^+/CH_4 system has been extensively explored by means of diverse experimental and theoretical methods.[12,18,36−38] Essentially, all studies agree that the global minimum corresponds to the inserted species H–Pt–CH$_3^+$ and that all barriers separating it from the products, $PtCH_2^+$ and H_2, lie below the entrance channel. On the basis of their observation of reaction 6a up to $n = 9$, Bondybey and co-workers have suggested similar potential-energy surfaces also for the platinum clusters Pt_n^+.[9] Considering the importance of reaction 6a as a model for methane activation,[39] we have revisited it up to $n = 5$ and found good agreement with the previous results (Table 2). Especially, we can fully confirm the anomalously low reactivity of the tetramer. According to preliminary DFT calculations of Bondybey and co-workers, Pt_4^+ has a tetrahedral structure and, thus, a relatively high degree of coordination, which might also raise the activation barriers with respect to H_2 elimination as these authors argue. However, we have now found that also the reverse reaction to H_2 elimination takes place, reaction 7, whereas $Pt_nCH_2^+$ clusters ($n = 2, 3, 5$) do not react in this manner.

$$Pt_4CH_2^+ + H_2 \rightarrow Pt_4^+ + CH_4 \qquad (7)$$
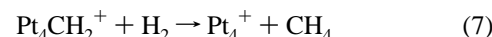
The ratio of rate constants allows the determination of the corresponding equilibrium constant, $K = k(6a, n = 4)/k(7) = 0.9 \pm 0.4$ and, thereby, the free reaction enthalpy, $\Delta_rG°(298$ K$) = 0 \pm 2$ kJ mol^{-1}. Hence, we conclude that the lack of a thermodynamic driving force is an important factor contributing to the low efficiency of reaction 6a in the case of the tetramer. This conclusion also is consistent with the finding of Hanmura et al. that for the tetramer reaction 6a is not anomalously slow at 0.15 eV collision energy, as the provision of kinetic energy is supposed to compensate for the insufficient thermodynamic impulsion of the reaction.[12] Note that the $\Delta_rG°$ value determined does not reflect thermochemistry only, but that also entropy changes play a role, as one vibrational degree of freedom is transformed into a rotational one in the reverse reaction. Considering the much lower rotational excitation energies, this

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TABLE 2: Bimolecular Rate Constants k and Efficiencies φ for the Addition/Elimination Reactions between Pt_n^+ and CH_4, NH_3, and N_2O, Respectively

reaction	n	k/cm^3 s^{-1} ^{a}	k_{lit}/cm^3 s^{-1}	lit.	$\varphi = k/k_c$ ^{b}
$Pt_n^+ + CH_4 \rightarrow Pt_nCH_2^+ + H_2$	1	5.0×10^{-10}	$(4.6 \pm 0.3) \times 10^{-10\,c}$	9	0.51
	2	8.2×10^{-10}	$(7.0 \pm 0.6) \times 10^{-10}$	9	0.85
	3	6.0×10^{-10}	$(8.7 \pm 0.7) \times 10^{-10}$	9	0.63
	4	1.5×10^{-11}	$(2.7 \pm 0.7) \times 10^{-11}$	9	0.02
	5	8.8×10^{-10}	$(1.1 \pm 0.2) \times 10^{-9}$	9	0.93
$Pt_nCH_2^+ + CH_4 \rightarrow Pt_nC_2H_4^+ + H_2$	1		$(2.0 \pm 0.7) \times 10^{-11}$	19	0.02^d
	5	2.5×10^{-10}			0.26
$Pt_n^+ + NH_3 \rightarrow Pt_nNH^+ + H_2$	2	5.4×10^{-10}			0.27
$Pt_nNH^+ + NH_3 \rightarrow NH_4^+ + Pt_nN$	2	6.6×10^{-10}			0.33
$Pt_n^+ + N_2O \rightarrow Pt_nO^+ + N_2$	1		$(7 \pm 2) \times 10^{-11}$	21	0.10^d
	2	$\leq 2.0 \times 10^{-13}$			$< 3.0 \times 10^{-4}$
	3	5.5×10^{-12}			1.3×10^{-3}
	4	$\leq 3.0 \times 10^{-13}$			$< 5.0 \times 10^{-4}$
	5	1.6×10^{-11}			0.02
$Pt_nO^+ + N_2O \rightarrow Pt_nO_2^+ + N_2$	1		$(1.9 \pm 0.6) \times 10^{-10}$	21	0.27^d
	3	1.2×10^{-11}			0.02
	5	5.8×10^{-11}			0.09

^{a} Errors estimated at $\pm 30\%$ for both CH_4 and N_2O and $\pm 50\%$ for NH_3. ^{b} Collision rates calculated according to capture theory.[33] ^{c} Compare with $k = 3.9 \pm 1.0$ (Irikura, K. K.; Beauchamp, J. L. *J. Phys. Chem.* **1991**, *95*, 8344), 5.9 ± 2.5 (ref 18, revised according to ref 38), and 7.6 ± 1.7 (ref 38, for $E_{kin} = 0.05$ eV), all values in 10^{-10} cm^3 s^{-1}. ^{d} Here: $\varphi = k_{lit}/k_c$.

change is supposed to increase the system's sum of states, thus favoring reaction 7 compared to 6a.

$$Pt_nCH_2^+ + CH_4 \rightarrow Pt_nC_2H_4^+ + H_2 \quad (6b)$$

With respect to the potential coupling of methane with other substrates, we also examined the secondary reaction 6b because of its possible relevance as a process competing with methane functionalization via $Pt_nCH_2^+$. However, reaction 6b only was observed for $n = 1$ and 5, for the former with rather low ($\varphi = 0.02$)[19] and for the latter with significantly higher efficiency ($\varphi = 0.26$). Compared to $Pt_nCH_2^+$, $n = 2-4$, the distinct reactivity of the monomer can be explained by the larger number of open coordination sites in a single Pt atom, which are obviously still not all occupied after addition of the first CH_2 fragment; in the product, however, the coordination number is somewhat reduced again because both methylene entities combine to one ethylene molecule.[20] The pentamer, on the other hand, already appears large enough that addition of the first CH_2 fragment does not alter the geometric and electronic structures of the cluster drastically so that reaction with a further methane molecule can occur at another Pt center. Bondybey and co-workers also reported adsorption of a third CH_4, resulting in $Pt_5C_3H_8^+$,[9] this reaction presumably being accompanied by termolecular stabilization. As expected, such simple association reactions become more important for larger clusters and higher pressures.[3,7]

Similarly to reaction 6a, the platinum dimer Pt_2^+ induces also dehydrogenation of NH_3, reaction 8a. The resulting ionic product, Pt_2NH^+, then transfers its proton to a further NH_3 molelcule, reaction 8b.

$$Pt_2^+ + NH_3 \rightarrow Pt_2NH^+ + H_2 \quad (8a)$$

$$Pt_2NH^+ + NH_3 \rightarrow NH_4^+ + Pt_2N \quad (8b)$$

Why does only the dimer undergo this reaction? It is interesting to note that a similar case has been reported for rhodium clusters Rh_n^+. Whereas neither the monomer nor the trimer or larger clusters Rh_n^+ react with methane, the dimer efficiently yields the corresponding carbene $Rh_2CH_2^+$ in analogy to reaction 6a.[40] A rationale for this strongly size-specific reactivity could be that a metal dimer, thanks to its lower degree of coordination,

possesses a higher intrinsic potential for bond activation than the larger clusters. Compared with the monomer, the dimer ion presumably gains more energy from the initial interaction with the substrate, thus helping to surmount the critical reaction barriers and suffice the thermochemical requirements associated with dehydrogenation. Moreover, the presence of two metal atoms that can form bonds toward the divalent dehydrogenation fragment, i.e., CH_2 or NH, respectively, is expected to enhance stabilization of the product and thereby further assist in its generation. In the case of the reaction between Pt_2^+ and NH_3, the product may be thought of as an imine. The increase in acidity well-known to be associated with the change from sp^3 to sp^2 hybridization indeed agrees with the consecutive protolysis, which is observed for Pt_2NH^+, reaction 8b, but not for $Pt_nNH_3^+$ ($n = 1, 3-5$).

Whereas all reactions described so far used low-energetic substrates that are generally not easily activated, this classification certainly no longer holds true for nitrous oxide, the next compound discussed. The reason we chose to include this substrate in our work is the existence of data for the reactions of N_2O with cationic platinum monomer[21] and small anionic platinum clusters,[13] which demand a comparison with the reactivity of Pt_n^+ clusters. As expected, N_2O reacts with Pt_n^+ by oxygen-atom transfer, reaction 9.

$$Pt_n^+ + yN_2O \rightarrow Pt_nO^+ + (y-1)N_2O + N_2 \rightarrow \rightarrow$$
$$Pt_nO_y^+ + yN_2 \quad (9)$$
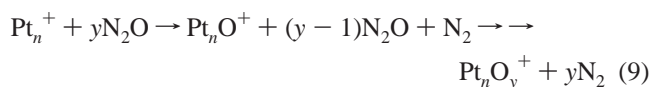
With respect to thermodynamics, reaction 9 is highly favorable because both a relatively strong metal–oxide bond is formed and the particularly stable N_2 molecule is released. However, the rate constants actually observed for the primary reaction are rather low for the different cluster sizes examined (Table 2). For the dimer and tetramer, the occurrence of reaction 9 could not be established at all ($\varphi < 5 \times 10^{-4}$), and even the most reactive species, i.e., atomic Pt^+, does not exhibit an efficiency higher than $\varphi = 0.1$.[21] Systematic studies by Armentrout et al.[41] and Schwarz and co-workers[42] suggest that the effectiveness of barriers is quite a general phenomenon for O-atom transfer from N_2O to transition-metal cations M^+. The qualitative explanation put forward by these authors[41,42] notes that the ground states of cationic oxides MO^+ correlate with

TABLE 3: Bimolecular Rate Constants k and Efficiencies φ for the Fragmentation Reactions of Pt_n^+ Exposed to O_2

| reaction	n	$k/\mathrm{cm^3\,s^{-1}}$ [a]	$\varphi = k/k_c$ [b]
$Pt_n^+ + O_2 \rightarrow Pt_{n-1}^+ + PtO_2$	2	1.3×10^{-10}	0.23
	3	7.6×10^{-13}	1.4×10^{-3}
	4	1.4×10^{-10}	0.25
	5	5.8×10^{-10}	1.1
$Pt_n^+ + O_2 \rightarrow Pt_{n-1}O^+ + PtO$	3	7.0×10^{-14}	1.0×10^{-4}
$Pt_n^+ + O_2 \rightarrow Pt_{n-1}O_2^+ + Pt$	3	5.0×10^{-13}	9.0×10^{-4}

[a] Errors estimated at ±30%. [b] Collision rates calculated according to capture theory.[33]

atomic $O(^3P)$ whereas adiabatic oxygen release from N_2O yields $O(^1D)$, so that the overall reactions leading to MO^+ in their ground states are formally spin-forbidden. Although the potential-energy surfaces of the joined systems, $M^+ + N_2O$, are certainly much more complicated,[43] particularly if not only single metal atoms but clusters are involved, there is experimental evidence that barriers indeed are a common feature of reactions between M_n^+ and molecules XYZ being isoelectronic with N_2O.[44,45] For the reactions of N_2O and anionic transition-metal clusters, the situation is complex, too. Whereas Pd_n^- clusters induce O-atom transfers with high efficiencies, the analogous reactions are strongly size-selective in the case of Pt_n^-. Hintz and Ervin found the trimer and the hexamer to be more than 1 order of magnitude less reactive than the other clusters investigated ($n = 3-7$).[13] Probably, a detailed understanding of O-transfer in reaction 9 and the related problems has to await substantial progress in the theoretical treatment of platinum clusters.

Secondary O-atom transfers were observed up to $y = 2$ for $n = 1$ and 5 and $y = 3$ for $n = 3$, reaction 9. In the case of the trimer and pentamer, these numbers should not necessarily be considered as the saturation level, but they nevertheless suggest that any possible further consecutive reactions are rather inefficient. For the monomer, labeling experiments gave strong evidence for an inserted structure $OPtO^+$, thus explaining the absence of a third O-transfer, which would result in an unreasonably high oxidation state of platinum.[21] Remarkably, in all cases the secondary O-transfer occurs significantly more efficiently than the primary one, indicating that the barriers associated with the former are less pronounced. Finally, in the course of the experiments also some cluster fragmentation was observed, which was attributed to contamination by O_2, although its partial origin from reaction with N_2O cannot be excluded.

Addition/Degradation. This reaction mechanism becomes operative if the interaction between the cluster and the substrate is highly exothermic and expulsion of a cluster fragment is the energetically least demanding exit channel. Such a reaction is observed to take place between platinum clusters Pt_n^+ and dioxygen, reaction 10a.

$$Pt_n^+ + O_2 \rightarrow Pt_{n-1}^+ + PtO_2 \tag{10a}$$
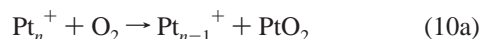
Although the neutral product PtO_2 cannot be detected, its generation rather than that of the separated atoms is unambiguous because the latter process would imply the occurrence of an endothermic reaction. Interestingly, the rate constants show a marked dependence on cluster size (Table 3). Whereas Pt_n^+ clusters, $n = 2$, 4, and 5, react fast (for the pentamer, unity efficiency is reached), the trimer reacts more than 100 times more slowly. Unfortunately, the present experiments do not suffice to distinguish whether this is a kinetic or a thermodynamic effect. In the absence of considerable barriers, the drastic decrease in efficiency would reflect a particular thermochemical stability of Pt_3^+, speculatively because of special geometric

features of this cluster size. Notably, the tetramer does not behave anomalously in its reaction with O_2, unlike that with CH_4 (see above). Hence, size-selective reactivity appears to depend crucially on the particular substrate in the case of platinum clusters, so that general conclusions based on the reactions with a single substrate might be misleading.

Another interesting aspect of reaction 10a is related with the oxygen distribution in the products. Taking into account that the reaction passes through the transient collision complex $Pt_nO_2^+$, the final elimination step can be considered as a disproportion. This behavior resembles the chemistry of platinum in solution where Pt^{IV} is well-known to be generally more stable than Pt^{II}. Other product channels have only been observed in the case of the trimer, reactions 10b and c. Note, however, that these are even less efficient than reaction 10a for $n = 3$.

$$Pt_3^+ + O_2 \rightarrow Pt_2O^+ + Pt \tag{10b}$$

$$Pt_3^+ + O_2 \rightarrow Pt_2O_2^+ + Pt \tag{10c}$$
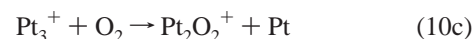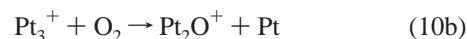
In the case of the Pt^+ monomer, simple addition of O_2 has been observed under flow-tube conditions.[46] Despite the higher probability of termolecular stabilization in these experiments, the association efficiency was as low as $\varphi = 3 \times 10^{-4}$. Moreover, chemisorption of O_2 as well as fragmentation has been observed for the anionic clusters Pt_n^- in flow-tube experiments.[13] Fragmentation predominated for the smallest cluster sizes studied, namely the trimer and the tetramer. In the case of the former, the overall reaction rate was much lower than that for the other clusters, similarly to the situation for its cationic homologue. However, without having further data for comparison, the implications of this finding remain unclear.

IV. Conclusions

Combined with previous work, the data provided in this study allow several comparisons. First, the reactivity of Pt_n^+ clusters can be contrasted with that of the Pt^+ monomer. Neglecting degradation reactions, which are naturally only possible for the clusters, we are left with mere association and addition/elimination reactions. The efficiencies of the former strongly increase when going from the monomer to the larger clusters because of lifetime effects. As their importance is quite a general phenomenon in cluster studies performed in the highly diluted gas phase, they do not point to a peculiarity inherent in platinum, however. The reactions with CH_4 and N_2O, respectively, are similar in the case of atomic Pt^+ and Pt_n^+ clusters, which indicates that their occurrence does not significantly depend on the ion's charge density. The same conclusion can be inferred from the reactions of these substrates with anionic Pt_n^- clusters:[9,13] although the efficiencies differ, the products formed are analogous to those generated from Pt_n^+.

With respect to the postulated potential of transition-metal clusters as model systems for the condensed phase, a comparison between the reactions studied here and those taking place at the surface of bulk platinum is even more warranted. In the case of H_2, the dissociative chemisorption observed to occur on Pt_5^+ indeed reflects the analogous process known for the condensed phase[47] and the same holds true regarding the activation of methane.[48] A more complicated picture emerges for the reactions between platinum and NH_3. Whereas most of the clusters investigated simply add NH_3 in the primary reaction, a remarkable exception is the dimer Pt_2^+, which readily effects dehydrogenation. Notably, platinum crystal faces predominantly adsorb molecular NH_3 but also induce dissociative chemisorp-

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tion whose efficiency strongly depends on the structure of the Pt surface.[49,50] However, dissociation of NH_3 does not stop at the stage of the imine but continues toward total decomposition of the substrate, eventually followed by desorption of N_2 and H_2, a process apparently not operative in the case of Pt_2^+. Interestingly, at $T > 1200$ K, free NH radicals were observed to be formed upon exposure of pure Pt to NH_3, which implies dehydrogenation of the substrate in a previous step.[51] Considering the presumably high interaction energy between Pt_2^+ and NH_3 (compare $D_0(Pt^+-NH_3) = 310$ kJ mol^{-1}),[19] which is distributed over a limited number of internal degrees of freedom, a high effective temperature results for the transient complex, thus rationalizing the similar reactivities. In the case of Pt_4^+ and Pt_5^+, activation of NH_3 only occurs after adsorption of several substrate molecules. Translated into the condensed phase, this would correspond with NH_3 activation beginning at higher coverage only; a phenomenon so far unknown in surface studies.

Concerning the reactivity of platinum surfaces toward N_2O, earlier studies at low temperatures found adsorption to be inefficient and accompanied by a minor extent of decomposition only.[52,53] In contrast, application of higher N_2O pressures at 363 K lead to formation of a complete oxygen monolayer on the Pt surface.[54] As O-atom transfer also occurs in the reactions between N_2O and Pt_n^+, another analogy connecting Pt clusters and surface chemistry evolves. The fact that N_2O decomposition on bulk Pt does not take place at low temperatures might point to barriers being operative that are probably also important in the corresponding reactions of Pt_n^+.

Finally, cluster fragmentation observed in the reactions with O_2 implies that the interaction between Pt_n^+ and O_2 releases enough energy to degrade the metal cluster, thus only being consistent with an inserted structure of the intermediate $Pt_nO_2^+$ complex. Accordingly, a recent DFT study predicted Pt_3^+ to cleave the O−O bond on energetic reasons.[55] For Pt crystal faces, dissociative chemisorption of O_2 is well-known to predominate at $T > 150$ K.[56−58] In marked contrast to the situation encountered in gas-phase studies of Pt clusters, however, the reaction energy released can be dissipated by the solid, thereby preventing surface degradation. Interestingly, at $T > 1000$ K, the Ostwald catalysts used to oxidize NH_3 by O_2 lose Pt, which indeed was rationalized by generation of PtO_2 (g).[59,60]

As a conclusion, we find that small Pt_n^+ clusters exhibit a reactivity resembling that of platinum surfaces. Hence, studying the reactions of these clusters as models for the far more complex processes of heterogeneous catalysis appears to be a reasonable approach in the case of platinum. Yet, one must not forget the specificities of certain Pt_n^+ clusters. In the reactions with CH_4, NH_3, and O_2, anomalous reactivities were observed for a single cluster size in each case, thus indicating size-specific electronic or geometric effects that have been inferred for other transition-metal clusters as well. For platinum, however, the situation seems to be particularly complicated as the exceptional cluster size differs in each reaction. Further experimental and also theoretical work is necessary to elucidate the origin of this behavior.

Other future studies should address the reactivity of platinum clusters related to more complex questions arising from heterogeneous catalysis. For example, most of the real catalytic processes involve more than a single substrate, thus substantially increasing the system's intricacy and therefore rendering the application of gas-phase models especially useful. Thanks to its superior ability in performing MS^n experiments and its ultrahigh mass resolution, FT-ICR mass spectrometry certainly will continue to play an important role in research devoted to platinum clusters and their reactivity.

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