Conclusions

In this work we have demonstrated, for the first time, the effect of pressure on the peak position of the surface plasmon resonance of colloidal gold and silver particles. For the citrate-derived particles, the observed red shifts and differential behavior of silver vs gold can be interpreted in terms of a free-electron gas model. For the particles prepared by the Faraday method, the pressure-induced peak shifts appear to reflect the much smaller average particle size obtained by this procedure. These results provide evidence that "pressure-tuning" can detect the appearance of a quantum size effect in these metal colloids.

Acknowledgment. This work was supported by grants from the National Science Foundation (DMR 86-12860) and Materials Science Division of the Department of Energy (DE-AC02-76ER01198). The authors thank Peggy Mochel of the Center for Microanalysis of Materials of the University of Illinois (supported under the above DOE contract) for valuable assistance with the electron microscope measurements.

Registry No. Au, 7440-57-5; Ag, 7440-22-4.

Supplementary Material Available: Tables of variances from least-squares fitting of absorption spectra, log-probability plots for each colloid, a plot of normalized pressure-induced changes in the dielectric constant of water, and a graph of the shifts of the Fermi level of gold and silver with increasing pressure (12 pages). Ordering information is given on any current masthead page.

Methane Activation on Unsupported Platinum Clusters

D. J. Trevor,[*,†] D. M. Cox,[*] and A. Kaldor

Contribution from Exxon Research and Engineering Company, Annandale, New Jersey 08801.

Received March 14, 1989

Abstract: We report the first observation of size-selective methane activation by unsupported platinum clusters. Platinum dimer through pentamer are the most reactive. The other small clusters, Pt_{6-24}, are less reactive. A factor of 4 drop in reactivity occurs in going from Pt_5 to Pt_6. The dominant products observed are of the form $Pt_nC_{1,2}H_y$. As the clusters increase in size, the number of hydrogens retained also increases. The reactivity tends to decrease with increasing cluster size, in contrast to the trends observed for dihydrogen chemisorption on several transition metals. A mild correlation is found between reactivity and the ability of certain size clusters to form compact structures and the number of ≤3-coordinated surface atoms in close-packed structures found to be most stable from theoretical calculations. These results suggest that, as in organometallic chemistry, coordinative unsaturation is critical for methane activation by naked metal clusters.

Advances in unsupported metal cluster synthesis[1] and characterization methods,[2] combined with the ability to study chemical reactivity,[3] have resulted in a significant increase in the type of systems studied and the amount of information gained. We have demonstrated that ionization potentials, magnetic moments, and chemical reactivity of unsupported metal clusters can be measured and frequently follow nonmonotonic trends from atomic to bulk properties.[4] Such experiments offer a rather direct approach to increasing our understanding of fundamental properties in the transition from molecular to metallic behavior.

Specifically, we have studied the reaction of methane with platinum clusters containing up to 24 atoms. Under our experimental conditions we have found them to activate C–H bonds in methane with certain size clusters being more reactive than others. Provided that our detection is nondestructive, we observe that (1) chemisorbed species are produced at a low extent of reaction whose hydrogen content only slightly varies with cluster size and (2) products produced at high reactant concentrations appear to chemisorb methane with significantly less hydrogen loss. The small clusters undergo facile chemistry not previously observed for either the atom or the bulk. Pt_{2-5} are more reactive than the atom by at least 1 order of magnitude and the bulk by probably several orders of magnitude. Nonmonotonic reactivity is observed to 24 atoms (the largest cluster studied). This is one of the few examples with unsupported transition-metal clusters in which the small clusters are found to be the most reactive species. At low extent of reaction, metal monocarbide peaks are observed for the atom and dimer suggestive of complete dehydrogenation. As the cluster size increases the extend of dehydrogenation decreases, since product peaks consisting of a combination of carbide and $-CH_m$ species are detected. At high extent of reaction, the metal carbide, or $-CH_m$, species appear to continue to chemisorb methane but with minimal dehydrogenation.

Matrix isolation studies of metal atom chemistry have failed to find a ground-state atom,[5] with the possible exception of aluminum,[6,7] that activates methane. However, alkanes including methane are rather easily activated by partially coordinately unsaturated metal centers in many organometallic complexes.[8]

[†] Present address: AT&T Bell Laboratories, Murray Hill, NJ 07974.

(1) Dietz, T. G.; Duncan, M. A.; Powers, D. E.; Smalley, R. E. *J. Chem. Phys.* **1981**, *74*, 6511. Bondybey, V. E.; English, J. H. *Chem. Phys. Lett.* **1983**, *94*, 443–447. For a review of this field concentrated on spectroscopy see: Morse, M. D. *Chem. Rev.* **1988**, *86*, 1049–1109.

(2) As examples of physical property measurements see the following. (a) Ionization potentials: Rohlfing, E. A.; Cox, D. M.; Kaldor, A.; Johnson, K. H. *J. Chem. Phys.* **1984**, *81*, 3846–3851. (b) Magnetic moments: Cox, D. M.; Trevor, D. J.; Whetten, R. L.; Rohlfing, E. A.; Kaldor, A. *Phys. Rev.* **1985**, *B32*, 7290–7298. (c) Photodissociation: Brucat, P. J.; Zheng, L. S.; Pettiette, C. L.; Yang, S.; Smalley, R. E. *J. Chem. Phys.* **1986**, *84*, 3078–3088.

(3) (a) Trevor, D. J.; Whetten, R. L.; Cox, D. M.; Kaldor, A. *J. Am. Chem. Soc.* **1985**, *107*, 518–519. (b) Whetten, R. L.; Cox, D. M.; Trevor, D. J.; Kaldor, A. *J. Phys. Chem.* **1985**, *89*, 566–569. (c) Geusic, M. E.; Morse, M. D.; Smalley, R. E. *J. Chem. Phys.* **1985**, *82*, 590–591. (c) Morse, M. D.; Geusic, M. E.; Heath, J. R.; Smalley, R. E. *J. Chem. Phys.* **1985**, *83*, 2293–2304. (d) Richtsmeier, S. C.; Parks, E. K.; Liu, K.; Pobo, L. G.; Riley, S. J. *J. Chem. Phys.* **1985**, *82*, 3659–3665. (e) Parks, E. K.; Liu, K.; Richtsmeier, S. C.; Pobo, L. C.; Riley, S. J. *J. Chem. Phys.* **1985**, *83*, 2882–2888, erratum *J. Chem. Phys.* **1985**, *83*, 5353. (f) Cox, D. M.; Trevor, D. J.; Whetten, R. L.; Kaldor, A. *J. Phys. Chem.* **1988**, *92*, 421–429. (g) Zakin, M. R.; Cox, D. M.; Kaldor, A. *J. Chem. Phys.* **1988**, *89*, 1201–1202.

(4) Kaldor, A.; Cox, D. M.; Zakin, M. R. In *Evolution of Size Effects in Chemical Dynamics, Part 2*; Prigogine, I., Rice, S. A., Eds. Advances in Chemical Physics, Vol. 70; Wiley: New York, 1988; p 211.

(5) Billups, W. E.; Konarski, M. M.; Hauge, R. N.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7393–7394. Perutz, R. N. *Chem. Rev.* **1985**, *85*, 77–96.

(6) Klabunde, K. J.; Tanaka, Y. *J. Am. Chem. Soc.* **1983**, *105*, 3544–3546.

(7) Parnis, J. M.; Ozin, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 1699–1700.

(8) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Boston, 1984.

0002-7863/90/1512-3742$02.50/0

It is also well-known that platinum and many other metals carry out H/D exchange with methane and other alkanes near room temperature.[9] Because matrix studies mandate low temperatures, it is reasonable to assume that methane activation has a high barrier or very restricted transition state. This is also suggested from our earlier studies in which we found hydrogen activation but not methane activation on iron[3b] aluminum,[3f] and rhodium clusters.[3g] In the case of small platinum clusters, we observe methane activation with the small clusters having significantly higher rates than the large clusters.

Methane activation on tungsten and rhodium surfaces has been studied extensively in order to determine the mechanism of activation.[10] A molecular beam scattering study[11] of dissociative chemisorption of methane on the W(110) surface at 800 K found the reaction to be consistent with tunneling through a barrier of 27.5 kcal/mol. This model predicts the observed exponential dependence of sticking probability on the normal translational energy. The reported sticking probability at room temperature was less than 10^{-4}. A molecular beam surface study[12] of methane on Ni(111) also found an exponential increase in dissociation probability on the normal component of translational energy, which was interpreted to mean a high barrier. These observations imply a slow,[13] highly activated reaction of methane with metal surfaces. Our observations suggest that another mechanism is operable for small platinum clusters.

We will discuss the possible origin of the observed size-sensitive chemistry in terms of an electronic and a structural model. The former has been applied with reasonable success to iron-,[14] vanadium-,[15] and niobium-[16]cluster reactions with hydrogen. This model relates changes in rate constants to frontier orbital energies. Although the agreement is good, significant departures from the model at specific cluster sizes indicate that it is not the complete story, and details of the electronic structure and geometry are important.

Unfortunately, supporting experimental measurements of electronic properties such as ionization potentials, magnetic moments, or geometric structure are not currently available for platinum. In their absence we will compare our results to a recently reported extended Hückel calculation on platinum metal clusters.[17] The structural model we will develop is based on the concept of degree of coordinative unsaturation, which is frequently used in organometallic and surface chemistry. These two models do not fully explain our observations further emphasizing the need for additional experimental and theoretical studies.

Experimental Section

The pulsed metal cluster fast flow chemical reactor apparatus used to carry out these studies has been previously described.[3b] In summary, platinum clusters were produced by the condensation of a laser-vaporized plume of metal atoms entrained in a fast helium flow at 1–2 atm. The clusters produced in the helium flow were injected into a reactor tube, 1-cm diameter, 5-cm long into which a second pulse of methane diluted in helium was added. The resultant mixture underwent reactions at an estimated 0.03–0.01 atm[18] of total pressure for approximately 85 ± 15 μs. The experiments were performed by alternating pulses of reactant mixture and pure helium from independent reactor pulsed valves attempting to account for pulse to pulse variations and the significant effect (a factor of 2–4) the pure helium pulse had on the metal cluster signals. The method of alternating pulses, similar to that described by Geusic et al.[19] enabled accurate determination of the background (clean metal spectra), which was critical in determining the relative extent of reaction and the assignment of mass shifts due to products.

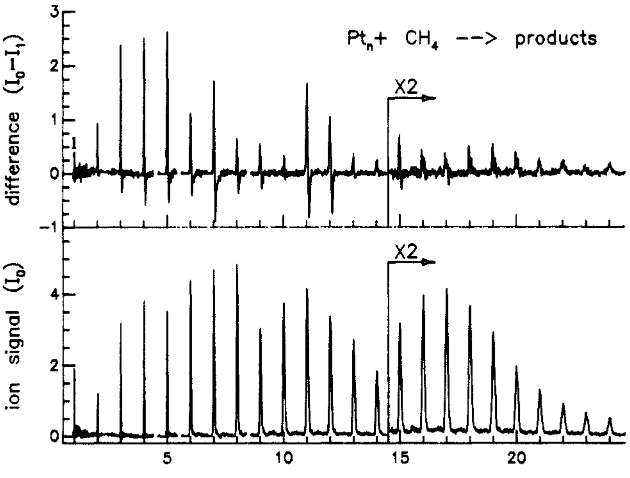

Figure 1. Lower frame: time-of-flight mass spectrum of platinum clusters before reaction with methane. Upper frame: difference between the lower spectrum and one obtained with 0.66% methane in helium. In the upper frame a positive signal indicates depletion of bare clusters while a negative signal indicates products.

The detection method was single-photon ionization with 10–50-μJ molecular fluorine excimer radiation at 7.87 eV in a 3 mm × 10 mm area. The ions were mass analyzed by time-of-flight mass spectrometry. Due to the high mass of the platinum clusters, several different transmission settings of the mass spectrometer are required to observe ions from the atom to Pt_{24}. The spectra were not corrected for variations in the transmission function since calculations of rate constants only involve ratios of bare cluster ion signals with and without methane injected into the reactor.

The specific concentrations of methane in helium used were 1.3%, 0.66%, and 0.37%. The reactant gas pulse was 5% of the total flow and overlapped in time with the main beam pulse. The turbulence induced by the addition of the second pulse of gas was assumed to thoroughly mix the reactant with the metal clusters. We have not yet developed a method to test this assumption. However, comparing our results for iron reactions with hydrogen[20] with previously reported studies of the same system,[3d] but carried out under laminar flow conditions, indicated that mixing due to turbulence was not complete, and the absolute rate constants reported here could be as much as 1 order of magnitude too small. Yet the relative rate constants should be accurate to about ±20%.

Time-of-flight measurements on the neutral beam are consistent with a 300–600 K range in translational temperature of the metal clusters entering the reactor. A significant temperature gradient must exist in the early stages of cluster production due to the quenching of the vaporized metal plume. By performing time-of-flight measurements with different production region lengths, the translational temperature of the clusters was found to be equilibrated by the time they enter the reactor. Geusic et al.,[19] with a similar apparatus, with a factor of 4 higher flow and higher resolution neutral time-of-flight measurements, had derived a "stagnation" temperature of 320 K. To be somewhat conservative and to simplify our discussion, we have chosen to assume a uniform temperature of 400 K for the reacting metal clusters. Hopefully further experimental measurements will be able to quantify the temperature and place these measurements on an absolute scale.

Results and Discussion

Figure 1 is a plot of the time-of-flight mass spectrum of platinum clusters out to Pt_{24}. The lower frame is the clean metal cluster mass spectrum with only helium pulsed into the reactor.

---

(9) Kemball, C. *Proc. R. Soc. (London)* **1953**, *A217*, 376–389. Gualt, F. G. *Adv. Catal.* **1981**, *30*, 1–95, and references therein.

(10) Rettner, C. T.; Pfnur, H. E.; Auerbach, D. J. *J. Chem. Phys.* **1986**, *84*, 4163–4167, and references therein.

(11) Rettner, C. T.; Pfnur, H. E.; Auerbach, D. J. *Phys. Rev. Lett.* **1985**, *54*, 2716–2719.

(12) Lee, M. B.; Yang, Q. Y.; Tang, S. L.; Ceyer, S. T. *J. Chem. Phys.* **1986**, *85*, 1693–1694.

(13) Yates, J. T.; Madey, T. E. *Surf. Sci.* **1971**, *28*, 437–459. Madey, T. *Surf. Sci.* **1972**, *29*, 571–589.

(14) Whetten, R. L.; Cox, D. M.; Trevor, D. J.; Kaldor, A. *Phys. Rev. Lett.* **1985**, *54*, 1494–1497.

(15) Kaldor, A.; Cox, D. M.; Trevor, D. J.; Zakin, M. R. *Z. Phys. D: At., Mol. Clusters* **1986**, *3*, 195–204.

(16) Whetten, R. L.; Zakin, M. R.; Cox, D. M.; Trevor, D. J.; Kaldor, A. *J. Chem. Phys.* **1986**, *85*, 1697–1698.

(17) Bigot, B.; Minot, C. *J. Am. Chem. Soc.* **1984**, *106*, 6601–6615.

(18) The pressure in the reactor was calculted with 3500 L/s for the effective pumping speed of the pump, baffle, and gate value combination for He, an ion gauge correction factor of 8, and the formula $P = F/AC$ where F is the flow of helium, A is the cross-sectional area of the reactor, and C is either the speed of sound or the measured average velocity (reactor length/residence time).

(19) Geusic, M. E.; Morse, M. D.; O'Brien, S. C.; Smalley, R. E. *Rev. Sci. Instrum.* **1985**, *56*, 2123–2130.

(20) Using our current characterization of the source and data reported in ref 14.

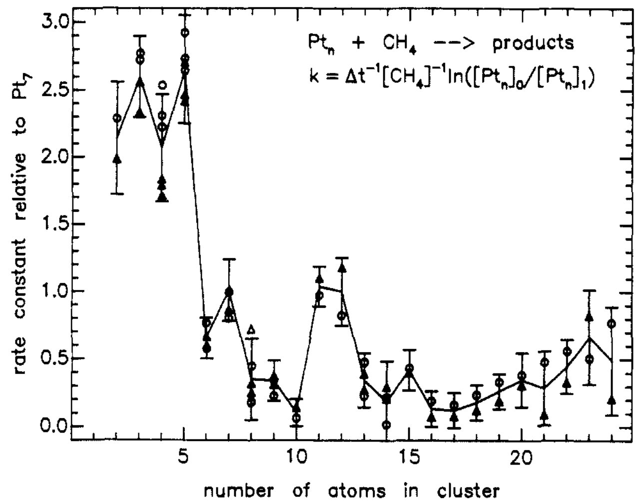

Figure 2. Rate constants relative to Pt_7 as a function of size for platinum cluster reactions with methane. The magnitude of the rate constant for Pt_7 is about 5×10^{-11} cm^3/s per molecule. The line is an average of several measurements, and the error bars indicate 1 standard deviation.

The upper frame is the difference between the clean spectrum I_0 and the spectrum observed after reaction with the 0.66% methane in helium mixture, I_1. This figure contains five separate data sets collected with different mass spectrometer transmissions. This variable transmission is the origin of the apparent intensity oscillation as a function of cluster size in the clean spectrum. By adjusting the deflection plate voltages that control this transmission function, mass spectra are optimized for Pt_3, Pt_5, Pt_8, Pt_{11}, and Pt_{17}. The data sets used to make Figure 1 range from Pt-Pt_4, Pt_5, Pt_{8-6}, Pt_{9-14}, and Pt_{15-25}.

Reaction rate constants are obtained by measuring the amount of unreacted metal. Reactor conditions are pseudo first order with excess methane.[21] The general reaction is

$$Pt_n + CH_4 \rightarrow \text{products} \qquad (1)$$

By integrating the rate equation for reaction 1, we obtain the usual first-order logarithmic dependence on the survival fraction. Since all metal clusters spend the same time in the reactor, $[CH_4]$ does not change significantly and the $[Pt_n]_1/[Pt_n]_0$ ratio is assumed to be equal to the ratio of ion signals with and without methane injected into the reactor; the rate constant for a particular size metal k_n is given by

$$k_n = \frac{-1}{[CH_4]\Delta t} \ln \frac{[Pt_n]_1}{[Pt_n]_0} \qquad (2)$$

This quantity is calculated from the data and plotted relative to k_7 in Figure 2. The larger amount of depletion easily observed in the mass spectrum for Pt_{3-5}, Pt_7, and $Pt_{11,12}$ shows the expected increase in their rate constants.

With the use of 85 ± 15 μs for Δt and 0.03 ± 0.01 atm for the total pressure, k_7 is found to have a value of $(5 \pm 3) \times 10^{-11}$ cm^3/s per molecule. The stated uncertainty of $\pm 3 \times 10^{-11}$ only accounts for the lack of accuracy in total pressure and residence time. The absolute value of these rate constants could still be inaccurate by up to 1 order of magnitude due to inadequate mixing or an overly simplified reaction mechanism. Even within these uncertainties the small platinum clusters react rapidly with methane. The value of k_7 is only 9% of the hard-sphere collision rate constant (from a collision diameter of 5 Å). This high probability of reaction places a maximum on the activation energy of 2 kcal/mol at 400 K.

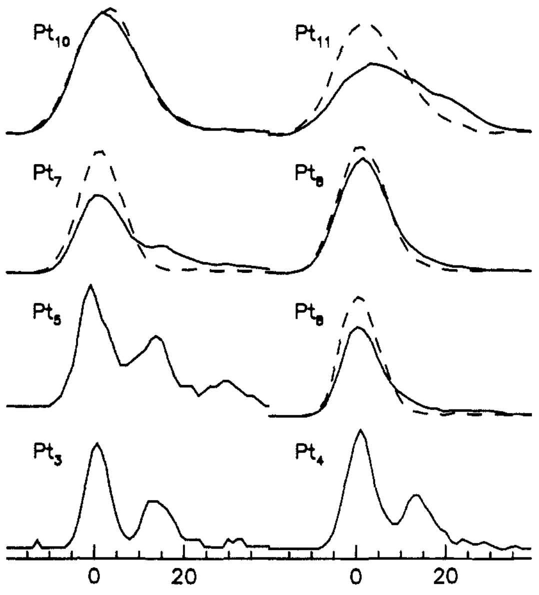

Figure 3. Plots of individual regions of the mass spectrum after reaction with 0.66% methane. For $Pt_{6-8,10,11}$ the clean metal spectrum is also plotted for comparison as dashed lines.

The observation of metal cluster depletion and the appearance of products in the mass spectrum we interpret as evidence for a chemical reaction. In the difference spectrum of Figure 1, the detected products (signal below zero) do not appear as intense as the loss in metal ion signal. We do not completely understand the cause of this phenomena, which seems to be particularly bad for platinum but has been observed to a lesser extent for a variety of reactions including CO[22] and O_2[3b] with transition metals and aluminum.[23]

One likely explanation is a significantly reduced product detection efficiency. The ionization potentials (IPs) of products are often observed to increase,[24] and we expect that to be the case here. The ionization cross section for almost all of the relevant species, once several electronvolts above threshold, should be of comparable magnitude.[25] But the ionizing photon energy is only slightly above the expected IPs of the small clean Pt clusters. This will likely result in some products not being detected at all, while others may not be detected as efficiently as the clean metal clusters.

Dissociative ionization can also interfere with these measurements. If the products dissociatively ionize all the way back to the clean metal cluster ions, they would produce an interference with the metal ion signals used to determine the reaction rate constants. In most cases this effect will reduce the apparent reactivity. With the product adiabatic IPs expected to fall in the 7-8-eV range, not much excess energy is available with 7.87-eV photons. Dissociative ionization thus appears unlikely and is assumed to have a negligible effect on the metal cluster ion signals.

As seen in Figure 2 a significant drop in reactivity occurs between Pt_5 and Pt_6, also Pt_{10} and to a lesser extent $Pt_{2,4,6,8,9,12,14,16}$ are less reactive toward methane than their neighboring clusters. The solid line plotted with error bars is an average of at least two separate measurements for each size cluster with two different concentrations. For the more reactive clusters, three different concentrations are used. The data scale, as expected from eq 2, is consistent with the pseudo-first-order assumption. Sample data points are plotted to show the variations observed and the re-

---

[21] Two independent methods have been used to estimate the metal partial pressure in the reactor. Each yields ~10^{-6} Torr of partial pressure for a particular size cluster. The methods used were based on (1) total mass of metal in the beam and an estimate of the distribution of this mass among the clusters or (2) the measured ion signal and estimating ionization cross sections and divergence of the molecular beam.

[22] Cox, D. M.; Reichmann, K.; Trevor, D. J.; Kaldor, A. *J. Chem. Phys.* **1988**, *88*, 111-119.

[23] Cox, D. M.; Trevor, D. J.; Whetten, R. L.; Kaldor, A. *J. Phys. Chem.* **1988**, *92*, 421-429.

[24] Zakin, M. R.; Cox, D. M.; Whetten, R. L.; Trevor, D. J.; Kaldor, A. *Chem. Phys. Lett.* **1987**, *135*, 223-228.

[25] For general discussions of photoionization: Berkowitz, J. *Photoabsorption, Photoionization, and Photoelectron Spectroscopy*; Academic: New York, 1979.

Table I. Product Ion Species Observed at Large Extent of Reaction[a]

formula	*m* major	*m* minor
$PtC(CD_4)_m$[b]	0, 4	5, 3
Pt_2C_m	1	
$Pt_2CD_2(CD_4)_m$	0, 2	3, 5
$Pt_3C(CD_4)_m$	0, 3	2
$Pt_4C(CD_4)_m$	0, 2, 1	
Pt_5C_m	1	2
$Pt_5CD_2(CD_4)_m$	2	
$Pt_6C(CD_4)_m$	0	2
Pt_6CD_2		

[a] Uncertainty of ±2 amu is assigned to the mass peaks observed. This results in most cases to an uncertainty of only ±1 in the number deuterium atoms. [b] Only PtC observed with CH_4.

producibility of these measurements.

The rate constant for the atom is not plotted in Figure 2. The ionization potential of the atom is 8.96 eV,[26] and thus the atom is not expected to be ionized with the 7.87-eV photons. Yet, a small signal is detected for the atom. This ion signal could be produced by either a two-photon ionization process that is detectable because of the high atom concentration in the beam or a single-photon ionization of an excited state (one possibility is $^3F_3$). If excited states are responsible for the observed signal then the rate constant measured is an unknown combination of electronic quenching and ground- and excited-state reactions. The measured rate constant for the atom is less than one-tenth the value observed for the dimer.

Figure 3 shows expanded plots of several of the mass spectral features observed for a mix of 0.66% methane in helium. For comparison purposes the clean metal spectra are also plotted in cases where the product peaks are not obvious. The widths of the product peaks are larger than those of the corresponding bare cluster peaks, indicating that the products are a combination of species differing in the number of hydrogen atoms. In spite of the variation in depletion mentioned above, the types of products observed change only slightly with cluster size. Multiple-carbon-containing products are observed for Pt_5, which is also the most reactive cluster. This contrast in product appearance disappears as the extent of reaction is increased by increasing the reactant partial pressure. At higher concentrations we can detect multiple-carbon-containing products on most metal clusters. This suggests that the subsequent reaction of the primary products is quite facile.

The product ions observed for the reactive metal clusters are generally highly dehydrogenated. In the following discussion, we assume that the photoionization laser used for detection does not photofragment the reaction products. This appears to be a reasonable assumption based on the photon energies used, but the energetics are not sufficiently well-known to be absolutely positive. The means of the major product mass peaks at low extent of reaction increase from 12 for Pt, 13 for Pt_3, to 14 for Pt_{11}. Our observed mass resolution limits us from obtaining directly the exact distribution of observed products. The width in mass due to the natural isotopic distribution[27] is comparable to our instrumental resolution for platinum, making product identification even more difficult. We have obtained these product masses by performing a linear least-squares fit of the observed product peaks on a mass scale, with functions derived from the clean metal peaks by shifting them appropriately to higher mass, assuming the chemisorbed products only contain carbon and hydrogen. Uncertainties of ±0.5 amu are assigned to the mean adduct masses.

The product masses at our highest concentration, 33% mixtures, are presented in Table I. CD_4 is used to help determine the adduct mass. In addition CH_4 is used to determine the stoichiometry for Pt_{2-4} adducts. For the platinum atom with CH_4, the only major product observed is PtC, whereas with CD_4 several other product ions are observed. The higher mass products on the atom with CD_4 are the weakest and most difficult to produce reliably, leaving the stoichiometry assignment questionable for $PtC(CD_4)_4$. An uncertainty of ±2 amu is assigned to the means of the product masses in Table I because low signals did not permit the fitting techniques to be used. The widths of the peaks indicate that the products have a distribution of deuterium content. The difference in products observed for CH_4 and CD_4 may be associated with a kinetic isotope effect in the dehydrogenation reactions.

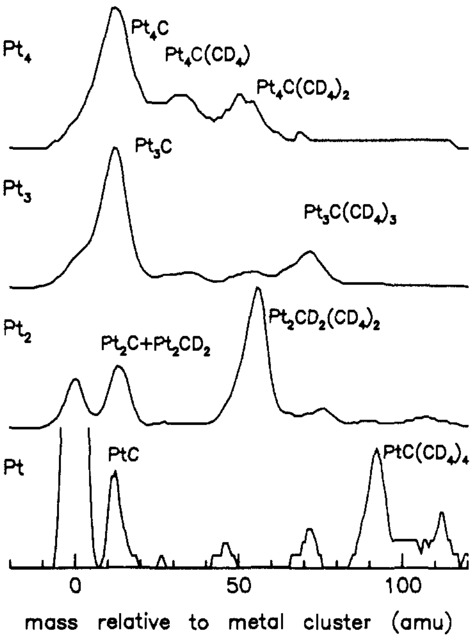

Figure 4. Time-of-flight mass spectrum of platinum clusters reacted with 33% methane-d_4 showing the series of methane adsorption products on the atom through the tetramer carbides.

Regions of the best mass spectrum obtained with 33% CD_4 are shown in Figure 4. The labeled peaks are those given under the column labeled major products, while the unlabeled peaks appear under the column titled minor products in Table I. The format used to describe the stoichiometry of the products is based upon the observation of a sequence of peaks, for example $Pt_4C(CD_4)_m$ where $m = 0$, 1, and 2 are all observed. This format suggests that chemisorption of methane on the metal cluster carbides proceeds with minimal loss of hydrogen.

Size Dependence. Heterogeneous catalytic chemical reactions are many times classified as facile or demanding with respect to metal dispersion,[28] where a demanding reaction refers to one that depends upon metal dispersion while a facile reaction is one that is independent of metal dispersion. Because dispersion specifies the fraction of surface atoms, it only indirectly relates to detailed structure.[29] However, structure is frequently associated with the origin of the demanding nature of a catalytic reaction. The correlation of ionization potentials with dissociative chemisorption of deuterium on iron clusters[14] points to an additional origin of the demanding nature of a chemical reaction on metal clusters, namely electronic.

Work on single-crystal surfaces has enabled detailed studies of structural effects in chemical reactions.[30] Even in these studies, crystal surface electronic and geometric effects cannot always be decoupled, as evidenced by work function variation with surface structure.[31] From an ab initio point of view, electronic structure

---

(26) Moore, C. E. *Atomic Energy Levels*; National Standard Reference Data Service, National Bureau of Standards Circular No. 35; NBS: Washington, DC, 1969.

(27) For a cluster of size *n*, the width of its mass peak will be $\sigma_n = n^{1/2}\sigma_1$ where σ_1 is the variance of the atomic distribution. For Pt $\sigma_1 = 1.136$.

(28) Boudart, M. *Adv. Catal.* **1969**, *21*, 153. Bond, G. C. *Surf. Sci.* **1985**, *156*, 966–981.

(29) Boudart, M.; Djega-Mariadasson, G. *Kinetics of Heterogeneous Catalytic Reactions*; Princeton University: Princeton, 1984, and references therein.

(30) For example: Somorjai, G. A. *Chem. Soc. Rev.* **1984**, *13*, 21–349.

(31) Holzl, J.; Schulte, F. K. *Solid Surface Physics*; Springer Verlag Series: New York, 1979; p 1–150. Smolvchowski, R. *Phys. Rev.* **1941**, *60*, 661–674. Rhead, G. E. *Surf. Sci.* **1977**, *68*, 20–38.

Table II

Pt$_n$ n	$(n, m)^a$ m	(EHT+SO)/n (eV)^b	IP (eV)^c	fraction with CN < 4^d	R (Å)^e
2	1	0.260	11.775	1	1.385
3	1	0.520	11.687	1	1.60
4	1	0.877	11.647	1	1.70
5	4	1.043	11.502	0.4	2.26
6	5	1.162	11.455	0	1.96
7	10, 3, 6	1.190	11.419	0.143	2.46
8	21, 24, 8, 1, 2, 4, 17, 16	1.209	11.394	0.17	2.76
9	20, 10	1.262	11.441	0	2.76
10	1, 35, 3 34, 36	1.290	11.306	0.04	2.88
11	2, 3, 1	1.327	11.306	0.03	2.63^f
12	2, 1, 5, 11	1.341	11.306	0.02	2.63^f
13	3, 23	1.385	11.299	0	2.77^f

^{a}Structure notation from the paper by BM.[17] Included are the structures that have an EHT+SO binding energy within 0.25 eV of the most stable. ^{b}The average value for the selected structures. ^{c}The negative of the Fermi energy for the most stable structures. ^{d}Fraction of the atoms in a given structure that have a coordination number (CN) less than 4 averaged over the selected structures. ^{e}Radius of the smallest cluster in the selected set of structures. $^f R$ is for the most compact structures (11, 15), (12, 6), and (13, 4).

governs geometric structure, making this distinction a mute point. Yet the success of predicting and understanding much of organic and inorganic chemistry based on geometric structure is difficult to overlook. At the foundation of using geometric structure to predict chemistry is the concepts of directional bonding and fixed valency. The problem is that metals, especially highly coordinatively unsaturated clusters, are not expected to be specific in bonding direction and/or valency.

As stated above, dispersion only indirectly relates to cluster structure and, for values near unity (i.e., highly dispersed systems), is not sensitive to cluster size. Our technique enables direct measurements of chemistry variation as a function cluster size, i.e., number of atoms. The small cluster region, near unity dispersion, is also expected to show the most dramatic changes in electronic structure. Therefore, these studies offer a unique opportunity to examine the demanding nature of chemical reactions in the cluster size range where the largest changes are expected.

Our search for understanding the observed demanding nature of methane chemisorption on platinum clusters is in two directions. First, we consider electronic effects, such as correlations of reactivities with ionization potentials or availability of an occupied or unoccupied molecular orbital with a particular symmetry. Second, we consider geometrical structure, such as the availability of a type of active site or degree of coordination that acts as the kinetic driving force.

Since very little is known experimentally about the structural or electronic properties of Pt$_n$ clusters, we will compare our results with the extended Hückel theory (EHT) calculations of Bigot and Minot (BM).[17] BM performed calculations on the 1-atom through the 13-atom cluster, examining a large number of possible structures based upon close-packed fcc/hcp geometries, packed tetrahedrons, and highly symmetric polyhedra. For most 8-atom and larger clusters no single structure was found to be especially stable but rather a set of several. For most comparisons we have chosen the cluster structures that lie within 0.25 eV of the most stable. These are listed in Table II with BM's notation.

Electronic Model. Hydrogen activation by metal clusters shows dramatic size variations. An anticorrelation between IP variations and chemical reactivity[14] was found for deuterium activation by larger ($n \gtrsim 8$) iron clusters, where the lowest IP metal clusters display enhanced ability to activate deuterium. This electronic effect is interpreted in terms of the ability of HOMO to contribute electron density to σ^* of D_2 and thus promote dissociative chemisorption. A direct correlation is observed for clusters containing less than eight atoms.[4] This electronic effect is attributed to electron donation from the σ of D_2 to the LUMO of the metal cluster.

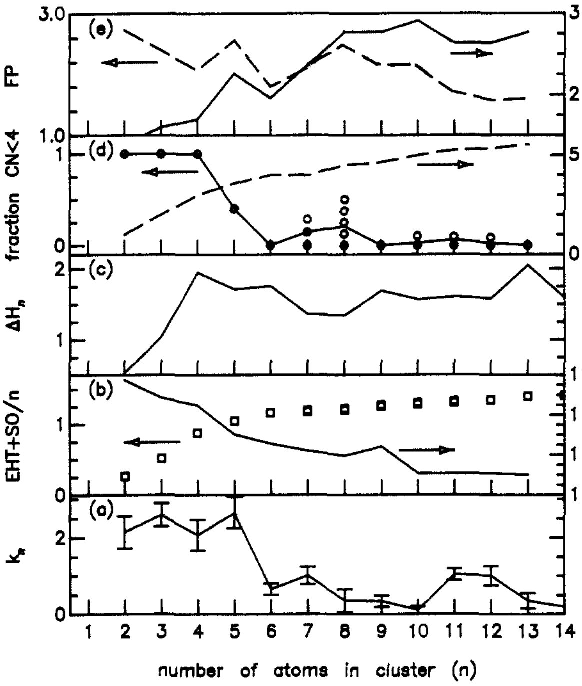

Figure 5. (a) Rate constants obtained in reacting platinum clusters with methane. For comparison with these data, several quantities from the calculation of BM are plotted in b–e. (b) EHT+SO energies per atom in electronvolts and the HOMO energies (IPs) of the most stable platinum clusters. (c) Heat of formation difference of the most stable platinum cluster, ΔH_n = EHT-SO(n) − EHT+SO(n − 1) in electronvolts. (d) Fraction of atoms with the CN less than 4 for the lowest energy set of structures (circles), plot of their average (solid line), and average CN of all atoms in the cluster (dashed line). (e) Factional packing FP (defined as the ratio of the volume of the sphere of the minimum radius that will enclose the cluster to the volume calculated from the bulk density) and the minimum radius of the most compact structures.

The correlation is explained in the following way. First, because the correlation is exponential in changes in IP of the clean metal cluster, a barrier to reaction in the entrance channel is suggested. The long-range interaction of the cluster with the closed shell of H_2 is repulsive because the metal cluster orbitals that are closest in energy and interact with the bonding orbital of H_2 are filled. At slightly shorter distances the σ^* orbital of H_2 (the LUMO of the reactant) and the HOMO of the cluster can interact. This attractive interaction can compensate for the initial repulsion and create a barrier. Since to a first approximation the IP measures the energy of the HOMO, the reaction barrier height will correlate with the energy difference between σ^* and the IP. This results in the anticorrelation of the reaction rate constant with exponential changes in IP for larger clusters.

Because the LUMO in methane is predicted to be several electronvolts higher in energy than σ^* in hydrogen,[32] it is likely that the barrier would be even greater. This greater activation energy makes the reaction too slow to be observed under our experimental conditions. Iron clusters, even out to 40 atoms in size, failed to activate methane.[3b] This is consistent with the idea of a larger barrier (>5 kcal/mol) for methane. Because platinum clusters have higher IPs than iron clusters, we expect these effects to be intensified.

This simplest model for hydrogen activation, however, fails for many clusters with fewer than 8 atoms. These clusters have significantly higher IPs than the larger clusters but activate hydrogen/deuterium at comparable rates. This points out that for the small clusters other interactions must play an important role.

We do not have experimental IP measurements for platinum clusters, and so we will compare our results with calculations

---

[32] Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic: New York, 1973. Hout, R. F.; Pietro, W. J.; Hehre, W. J. *A Pictorial Approach to Molecular Structure and Reactivity*; John Wiley & Sons: New York, 1984.

reported by BM. Within a one-electron picture, the IPs of the metal clusters are taken to be the negative of the EHT+SO (EHT with spin-orbit corrections) HOMO energies. The comparison made with the reactivity in Figure 5b does not show an anticorrelation. In fact the expected slow decrease in IP variations with cluster size[33] for low IP clusters predicts the larger clusters to be more reactive. This is not what is observed. The small high IP clusters carry out this chemistry most rapidly. This suggests the importance of other types of interactions more in analogy with organometallic complexes.[34]

One type of interaction that rationalizes small cluster reactivity empty or partially filled rather low-lying MO's with proper symmetry to accept electron density from the bonding orbital of the reactant.[35] If the symmetry is unique, so that the interactions are not abated by curve crossings, then we would predict a direct correlation with IP, that is, high IP corresponds to high reactivity. Not only will this type of symmetry restriction be harder to satisfy as cluster size increases, but the decreasing cluster IP will shut down the charge-accepting ability of the cluster. If this mechanism is active only for the small clusters, then the drop in reactivity of the larger clusters agrees with the prediction of a large barrier for methane activation as seen on clean metals. Without the symmetry restriction for high IP clusters we predict no correlation with HOMO energy and no significant barrier to reaction.

An important point of this model, which needs to be rationalized, is the origin of unfilled orbitals at or below the HOMO in energy. One calculation that makes similar predictions on nickel clusters shows evidence of a non-Aufbau filling of molecular orbitals to achieve the ground electronic state.[36] This implies that some of the d orbitals in a small cluster that lie below the HOMO in energy are not completely filled. Because of the higher directional character in bonding of the d orbitals than sp orbitals, interactions with unfilled d shell orbitals would have a rather unique symmetry. Partial coordinative unsaturation of a metal in an organometallic complex has a similar type of interaction.[34] This is because the majority of the orbitals are tied up in ligand bonding, leaving a unique partially filled orbital to interact with methane.

Within our guidelines of electronic effects, we conclude that methane activation on small platinum clusters does not follow the simplest model of metal donation to the antibonding orbitals of the reactant but some indication exists that the activation pattern might be explained in terms of partial charge donation from the HOMO of the reactant to low-lying unoccupied or partially occupied MO's of the metal cluster within the constraints of symmetry restrictions.

Geometric Model. We do not have a method at this time for characterizing or controlling the detailed geometric structure of small metal clusters. For a moment consider structure in a more general sense. Cluster size variations should result in significant changes in the structure of the surface of the metal clusters. Theoretical studies of the minimum energy geometry of metal clusters in this size range have yet to produce a simple picture of how clusters grow.[17] Calculations find no simple direction of attachment by a single atom onto a metal cluster that results in the most stable configuration for the adduct. Therefore, cluster growth involves significant rearrangements even for the addition of just one more atom. Rearrangement energies are calculated[17] to be less than the energy gained by the addition of an atom to the cluster. Complementary to this, these same calculations also do not predict a single stable structure for each size, but a group of structures differing in energy only by a fraction of that gained by addition of an atom. These considerations taken together suggest that, instead of a single structure, a set of structural isomers may be produced for each cluster size.

A few comments are in order concerning what is known about the structure of unsupported metal clusters. Studies of the extend of chemisorption on iron clusters[3d] suggest that these clusters are globular in shape. This was determined by measuring the extent of a chemical reaction pushed as far to completion as possible, analogous to a saturation coverage in surface science or the BET absorption methods in catalysis. The extent of reaction is obtained simply by measuring the number of ligands added to a specific size cluster. In this way the number of available sites in or on the cluster is counted. For hydrogen chemisorption on iron clusters the ratio of hydrogen atoms to the number of surface atoms, calculated assuming spherical-shaped structures, is found to be near 1. This technique, although it does not lend itself to detailed structure determination or is sensitive to simple distortions from a spherical geometry, may, in certain instances, distinguish globular from linear or planar structures. Also in support of the spherical structure assumption is the success of the jellium-type electronic models that have explained distinct maxima in mass spectra of gas-phase alkali clusters.[37]

Starting with globular clusters we can ask what type of surface structures might be expected. Because the smaller clusters (ones of interest here) do not have bulk periodicity, extended surface structures of high entropy and/or low stability such as rows and valleys can be ruled out. This leaves us with the lower energy surface structure of 3-fold triangular faces (111) (in fcc packing) and some 4-fold square faces (100). Calculation for larger metal clusters have shown that triangular faces should dominate for direction insensitive bonding.[38] In addition calculations have shown that starting from large known microcrystalline structures with 1000 atoms in fcc packing, all smaller clusters down to 12 atoms in size can be made by exposing just (111) and (100) faces.[39] Although these structures are not necessarily the lowest energy ones, it is interesting that they are all predicted to exist. These simple arguments limit the variety of surface structures available on clusters compared to single-crystal surfaces.

Size dependence of methane activation by Pt clusters, Figure 5a, suggests that less reactive clusters might be associated with compact, higher symmetry structures. Pt_n, for n = 4, 6, 8, 10, and 13, form relatively high symmetry, compact structure. Such compact structures also possess a smaller surface area and thus might exclude an active site that a less symmetric cluster, e.g., n = 3, 5, 7, 11, 12, and 15, might possess. In Figure 5e the radius of the minimum size sphere that can enclose a cluster is plotted as a function of cluster size. It shows minima at 4–6, and 8-atom clusters similar to the minima in the reactivity Figure 5a. To emphasize this point, also plotted in Figure 5e is the quantity called fractional packing (FP) where FP is the ratio of the volume of the sphere of minimum radius that can encompass the cluster to the volume expected on the basis of bulk packing. Although high-symmetry clusters result in the most dense packing, they are not in all cases the most stable but are still close in energy to that of the most stable cluster geometry.

The anticorrelation between high-density packing and reactivity suggests that the more fully coordinated atoms are less reactive. This is the usual consideration in organometallic chemistry and heterogeneous catalysis.[30,34,40] Figure 5d show the average coordination number (CN) of the metal clusters as a function of size. The CN is found to increase but begins to level off around Pt_5. By examining the CN of each atom in the group of lowest

---

(33) Kappes, M. M.; Schar, M.; Radi, P.; Schumacher, E. *J. Chem. Phys.* **1986**, *84*, 1863–1875.

(34) Albright, T. A. *Tetrahedron* **1982**, *38*, 1339–1388, and references therein.

(35) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026.

(36) Logan, J.; Newton, M. D.; Noell, J. O. *Int. J. Quantum Chem. Quantum Chem. Symp.* **1984**, *18*, 213–235.

(37) Knight, W. D.; Clemenger, K.; deHeer, W. A.; Saunders, W. A.; Chou, M. Y.; Cohen, M. L. *Phys. Rev. Lett.* **1984**, *52*, 2141–2143. Clemenger, K. *Phys. Rev.* **1985**, *B32*, 1359–1362. Clemenger, K.; Knight, W. D.; deHeer, W. A. Saunders, W. A. *Phys. Rev.* **1985**, *B31*, 2539–2540. Saunders, W. A.; Clemenger, K.; deHeer, W. A.; Knight, W. D. *Phys. Rev.* **1985**, *B32*, 1366–1368. Knight, W. D.; deHeer, W. A.; Clemenger, K.; Saunders, W. A. *Solid State Commun.* **1985**, *53*, 445–446. Chou, M. Y.; Cleland, A.; Cohen, M. L. *Solid State Commun.* **1984**, *52*, 645–648.

(38) Marks, L. D. *Surf. Sci.* **1985**, *150*, 358–366.

(39) Searcy, A. W. *J. Solid State Chem.* **1983**, *48*, 93–99. Hardeveld, R.; van Hartog, F. *Surf. Sci.* **1969**, *15*, 189–230.

(40) The more close-packed surfaces are less reactive toward H_2: Liu, R.; Ehrlich, G. *Surf. Sci.* **1982**, *119*, 207–233. Robota, H. J.; Vielhaber, W.; Lin, M. C.; Segner, J.; Ertl, G. *Surf. Sci.* **1985**, *155*, 101–120.

energy clusters as a function of size, a more significant effect is seen in the region around Pt_4–Pt_6. The fraction of atoms with CN less than 4 for each of the cluster structures in the lowest energy group is plotted in Figure 5d. The solid line is a simple average over the different structures in the most stable group. The change seen in this fraction as a function of cluster size correlates reasonably well with the reactivity pattern. Even averaging over more of the possible structures by increasing the energy criteria used to select them does not alter the general trend. A cutoff of 4 in CN agrees well with the most common valency of platinum compounds[41] but is significantly different from the metal where the bulk atom has a CN of 12 or even from a (111) surface atom that has a CN of 9.

If changes in the metal–metal bonding have an effect on methane activation, then a correlation between either the total bonding energy, EHT+SO shown in Figure 5b, or the ΔH_n, (EHT+SO(n) − EHT+SO(n − 1)) plotted in Figure 5c, would be expected. At this level of theory there appears to be no direct correlation between either the metal cluster bonding energy with another metal atom or its total bonding energy and the ability of the metal cluster to chemisorb methane. As pointed out by BM the coordination number and total energy also do not directly correlate due to the ability of the metal clusters to compensate for low coordination number by increasing individual bond strengths. Because metal–ligand bonding is stronger than individual the metal–metal bond,[41] the lack of a correlation is not too unexpected.

In fact, calculations of platinum cluster to hydrogen atom bond strengths show a significant drop in value in the same cluster size range as the fraction of atoms with coordination number less than 4.[42] This observation suggests that the reactivity variation is related to the exothermicity of the reaction. The Hammond principle[43] yields the same expectation, if we trust Pt_n–CH bond strengths to follow the theoretical trend for Pt_n–H. However, because significant changes in "structure" are expected from one size to the next in this small cluster regime, direct comparisons of rate constants and thermodynamics is tenous without a more quantitative model.[22]

We feel the correlation of the rate constant for methane chemisorption with the fraction of atoms with CN less than 4 is an example of how the degree of coordinative unsaturation controls the ability of platinum clusters to activate methane.

Products. Multiphoton absorption, dissociative ionization, and large changes in vertical ionization potentials will perturb the observed product mass spectra. Low ionization laser fluences were used to reduce the probability of multiphoton absorption. If extensive dissociative ionization (single or multiphoton) of the products occurred, it is reasonable that a bare metal cluster could be one of the fragment ions, making it impossible to completely deplete the clean metal cluster signals. In most cases the clean metal cluster signal can be entirely depleted by increasing the reactant concentration. This alone is not sufficient to rule out dissociative ionization,[44] which may still occur to some extent and contribute to uncertainties in product identification. However, we assume that dissociative ionization is not a major problem. Finally, if the ionization potentials of the products increase sufficiently, they will exceed the ionizing photon energy and not be detected. Such factors limit our ability to identify reaction products from just the observed mass spectra. In these experiments our highest photon energy available, 7.87 eV, was used in an attempt to minimize these problems. It is expected that experiments with tunable photon sources will help to further clarify product detection. Presently we assume that the product masses observed are parent ions and thus are representative of the neutral-chemistry reaction products.

The metal cluster single-carbon-containing species are the primary observed products. As the cluster size increases, the products go from PtC to $Pt_{11}CH_2$. We predict that very large particles or surfaces would likely produce CH_3 absorbed species. Methane activation on Ni(111) has been reported[13] to produce chemisorbed CH_3, which at least is consistant with our large cluster limit for Pt. These measurements are not directly sensitive to the degree of dissociation of the chemisorbed species, which makes structure identification impossible.

Direct carbide production from methane suggests a carbon to platinum cluster bond energy of more than 189 kcal/mol.[45] This exceeds the Pt–C dissociation energy by 44 kcal/mol.[46] The uncertainty in the detection mechanism for the atom signal also suggests that the products observed could result from an excited-state reaction. This would rationalize the conflict between the 189 kcal/mol value and the literature value for the atom. For the clusters ($n > 1$), the observation of Pt_n–C indicates quite strong bonds. The type of multiple bonding expected between the metal and the carbon atom is somewhat analogous to C_2 and C_3. The C–C bond energies in these species are 141 and 175 kcal/mol[47] while the Pt–C bond is 145 kcal/mol.[45] We predict strong bond energies for Pt_n–C, $1 < n < 6$, which might approach the upper bound of approximately 188 kcal mol. As n increases the amount of hydrogen retained also increases, suggesting that the Pt_n–C bond energy is decreasing making Pt_n–CH_2-type species preferred. Other possibilities that can explain the observations without requiring very strong Pt_n–C bond strengths are increasing Pt_n–H bond energies, dissociative ionization, and/or selective detection. Dissociative ionization can have a particularly bad effect on parent product identification. If, for example, the carbide species have low ionization potentials such that sufficient excess energy is available from the ionization process, cluster fission and/or H_2 elimination[48] could be induced by the detection process.

The HOMO in Pt–C is dominantly a Pt lone pair, which would imply only a small change in the vertical ionization potential compared to the platinum atom.[49] Again this would imply that the PtC species should not be single-photon ionized. For metal clusters, however, the HOMOs are more antibonding; thus, formation of σ bonds suggest an increase in the vertical ionization potentials. This has been demonstrated for hydrogen reactions with iron, vanadium, and niobium clusters.[24] Therefore, it is possible that the trend toward observing more hydrogen retention in the products as cluster size increases might be the result of changes in the ionization potentials, with the higher hydrogen content products requiring a larger cluster in order to be single-photon ionized with 7.87-eV photons.

At high extent of reaction, the major product species are listed in Table I. Unfortunately from the stoichiometry determined by mass spectroscopy, we are not able to identify a unique chemically significant sequence of products. There are several possibilities that arise from considering only the major products. Although the chemisorption appears to continue on the carbide with minimal loss of hydrogen/deuterium, it is still possible that methane is dissociatively chemisorbed. If one considers the methane adduct as methyl and a hydrogen atom, or methylene and a hydrogen molecule, the major products can be rewritten as follows: $Pt(CD_3)_5D$, $Pt_2(CD_3)_3D$, $Pt_3(CD_3)_4$, and $Pt_4(CD_2)_2$ and $Pt_4(CD_2)_2D_2$. The product species in this form result in "reasonable molecules" on all Pt_n species but the atom, which has high energy formal

---

(41) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Interscience: New York, 1972.

(42) Minot, C.; Bigot, B.; Hariti, A. *J. Am. Chem. Soc.* **1986** *108*, 196–206.

(43) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–338. Shustorovich, E. M. *Surf. Sci.* **1985**, *150*, L115–L121.

(44) For discussion of photoionization mass spectrometry on clusters see: Castleman, A. W., Jr.; Keesee, R. G. *Chem. Rev.* **1986**, *86*, 589–618.

(45) For the reaction $CH_4 + Pt_n \rightarrow C\text{–}Pt_n + 2H_2$ to be exothermic $-\Delta H$-(C–Pt_n) > ΔH_f (C(g) 171 kcal/mol) − ΔH_f (CH_4(g) −18 kcal/mol) which is 189 kcal/mol but D_0(Pt–C) = 145 kcal/mol.

(46) Ginerich, L. A. *Chem. Phys. Lett.* **1973**, *23*, 270–274.

(47) Stull, D. R.; Prophet, H. *JANAF Thermochemical Tables*, 2nd ed.; Natl. Stand. Ref. Data Ser.: Natl, Bur. Stand. No. 37: Washington, DC, 1971.

(48) Zakin, M. R.; Cox, D. M.; Kaldor, A. *J. Phys. Chem.* **1987**, *91*, 5224–5228. Zakin, M. R.; Brickman, R. O.; Cox, D. M.; Kaldor, A. *J. Chem. Phys.* **1988**, *88*, 5943–5947.

(49) Pt–C will have one strong σ and π bond and two completely nonbonding d orbitals. The HOMO obtained by EHT calculations is only slightly antibonding.

Pt(VI) state. Unfortunately this format does not account for the metal cluster carbide species. Other structures and mechanisms (such as dissociative ionization) exist that can explain these data, but more detailed experiments will be necessary to determine the answer.

Is This Something To Worry About? Dehydrogenation reactions on platinum and many other metal catalysts are not strongly demanding.[28-30,50] Our observations, to the extent that they are transferable to supported metal catalysts, show significant size sensitivity, and thus we would expect them to be demanding. We propose two explanations that might explain this discrepancy. The first is that the chemisorption step is not rate limiting in either H/D exchange or dehydrogenation. This is difficult to rationalize in light of the reported very small sticking probability for methane,[10-13] which suggests small rate constants for activation. The second explanation is that the size-dependent studies with supported clusters, due to the difficulty in stabilizing very small clusters, have not yet reached the very small cluster range. The majority of studies have used clusters with diameters of 10–20 Å, which for a spherical shape means >30 atoms. As seen from our data, the larger clusters appear to have smaller rates for chemisorption of methane than the 2–5-atom clusters.

We have not accomplished measurements of catalysis in this pulsed fast flow reactor but have studied the chemisorption of a reactant, the first step in any heterogeneous chemical process. This step for unsupported platinum clusters shows selectivity with respect to methane.

Another feature of these studies that is likely to be relevant to heterogeneous catalysis is the extent of this chemisorption previously reported for C_6 hydrocarbons with platinum.[3a] Unlike metal–surface studies under UHV conditions, which find a single benzene molecule bonded to several platinum atoms,[51] we have observed extensive chemisorption in which the number of absorbate molecules approach the number of metal atoms on the surface of the cluster. We believe this effect is the result of (1) the high-pressure conditions stabilizing intermediates, (2) the very high degree of coordinative unsaturation, and (3) the reduced steric hindrance for reactions on an isolated metal cluster surface compared to that on the flat metal. All of these effects must be considered when extrapolating surface science measurements to small clusters on supported catalysts.

The transferability of these results to supported catalysis is still in debate. Much of the work in catalysis attempts to isolate and/or miminize support effects: These experiments accomplish this by carrying out gas-phase experiments, but at the sacrifice of a collectible sample. Our observations that the electronic properties of clusters as a function of size are not simple extrapolations of bulk or atomic properties, and play a significant role in guiding gas-phase reactivity, should be transferable to heterogeneous catalysis. It is unlikely that the major IP changes seen for clusters will disappear once they are supported because ionization potentials of metal atoms strongly correlate with bulk work functions throughout the periodic table.

Conclusions

We report the first direct observation of methane activation by unsupported metal clusters. In addition, we find this reaction has a distinct cluster size dependence. We have identified a correlation of this reactivity pattern with high-density spherical close-packed structures and the number of ≤3-fold coordinated atoms by making comparisons with theoretical calculations. This leads to the suggestion that low-coordination metal atoms activate methane more readily than the more closely packed metal surface atoms. This is in accord with general interpretation of homogeneous catalysis and organometallic chemistry that coordinative unsaturation is a prerequisite to methane activation.[34]

The failure of the "simplest" electronic model to explain the size variation in reactivity indicates that mechanisms based solely on populating antibonding orbitals of adsorbates are not fully operable. For methane activation, which this model predicts to have a barrier for reaction, we find small metal clusters reacting without a significant barrier (<4 kcal/mol). Thus, the small clusters must have a way of circumventing this interaction. We present arguments that suggest the very small platinum clusters not only have high IPs, which makes them good charge acceptors, but also that they are distinct from the metal in d orbital occupancy due to the low coordination number of the metal atoms in the cluster. These hypotheses are attractive, but proof will require a much more thorough data base and additional calculations.

The type of products observed are correlated with the results of surface science and catalytic attempts to activate methane on metal and supported clusters. The observation of methane adsorption on the platinum carbide clusters suggests surface defects might be particularly critical in bulk surface methane activation studies.

Acknowledgment. The high-quality technical assistance of Ken Reichman was invaluable in getting these experiments performed in a timely and reproducible fashion.

Registry No. Pt, 7440-06-4; CH_4, 74-82-8; CD_4, 558-20-3.

---

(50) Davis, S. M.; Somorjai, G. A. *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis* King, Ed.; 1984; Vol. 4, pp 217-364.

(51) Salmeron, M.; Somorjai, G. A. *J. Phys. Chem.* **1981**, *85*, 3835-3840.