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FEATURE ARTICLE

Temperature Effects in Transition Metal Ion and Cluster Ion Reactions

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While reactions on the surface of bulk metal proceed in general under well-defined and experimentally easily measurable temperature and other conditions, this is usually not the case for reactions of metal atoms or clusters and their ions in high vacuum. A collision complex of the metal cluster with a polyatomic molecule (e.g., benzene) may be transiently stabilized by redistribution of the interaction energy, IVR. This energy redistribution results in heating of the collision complex to internal temperatures, which can be estimated to be often very high, but the data for its exact determination are usually not available. Semiquantitatively, the heat capacity of the complex will increase with the cluster size, and the temperature rise upon complex formation will correspondingly decrease. Such size-dependent heating effects are readily observable in FT-ICR studies of anionic and cationic cluster reactions, and when interpreting the data or trying to draw from it conclusions for bulk condensed phase reactions, they have to be taken into consideration. Conversely, the effect of such temperature rise in mass spectrometric studies can be decreased or eliminated, and the reactions of truly cold clusters can be investigated by "soft landing" the reactive molecule on a solvated cluster and exchanging it for inert ligands, e.g., argon atoms.

1. Introduction

Metal ions and more recently cluster ions stored in electromagnetic Fourier transform ion cyclotron resonance (FT-ICR) traps[1,2] permit convenient studies of their chemical reactions with a large variety of reactants,[3−8] and the ever increasing number of investigations in this field comes therefore as no surprise.[6,9−13] The high resolution of the FT-ICR technique allows unambiguous determination of the elemental composition of the investigated clusters, even in the presence of impurities with the same nominal mass. The ions can be stored in the trap with negligible losses for periods ranging up to many hours or even days. Furthermore, the reaction conditions can be well-defined and established, and the reactant pressure in the ICR cell is easily measured and calibrated. Even in cases when the pressure-measuring device is relatively remote from the cell, reliable calibration can still be accomplished by measuring rates of reactions whose rates are well established.[14]

The interest in cluster reactions stems to a large extent from the catalytic activity of transition metals,[15,16] and from their numerous applications in industry and technology. Transition metals, with their multitude of oxidation states and a dense manifold of electronic levels, are perhaps the most widely used industrial catalysts. The reactions of transition metal ions in ICR traps are therefore seen as suitable model systems for investigating their reactivity and their catalytic activity under well-defined experimental conditions.[7,17] A further advantage of such systems as opposed to the bulk is that a collision complex of a metal ion or ion cluster with the reactant species is sometimes sufficiently simple to be successfully modeled by theoretical ab initio calculations.[18−23]

Often overlooked in mass spectroscopic studies is the fact

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that even though the ions and ion clusters may initially be prepared translationally and internally cold, and the reactant pressure can be carefully measured and calibrated, in reality the effective internal temperature of a cluster−reactant collision complex in which the actual reaction takes place is usually not known, and not readily accessible to experimental measurement. This problem is particularly severe in FT-ICR work, where the collision rates ($0.01-1\ s^{-1}$) are some 7−10 orders of magnitude lower than for instance in guided ion beam or drift tube experiments. As the associative collision complex forms in the high vacuum, it is stabilized by internal redistribution of the binding energy (IVR). It is clear that such a complex will possess a considerable excess of energy, and its effective "temperature" must be quite different from that of the initial reactant ion cluster. It is easy to show that the resulting temperature can be very high and may have a crucial effect upon the further course of reactions. The temperature of reacting metal clusters, its changes during the reaction, and its effects upon the product formation are the main focus of this paper.

2. Long-Lived Collision Complex Formation and Its Temperature

Gas phase reactions in FT-ICR experiments usually proceed in ultrahigh vacuum of $10^{-8}-10^{-10}$ mbar. Under these circumstances the collision rates are of the order of $1\ s^{-1}$ or less, and in the absence of a "third body" which could stabilize the product, one might expect two-body recombination reactions of the type $A^{\pm} + B \rightarrow AB^{\pm}$ to be very inefficient. Somewhat surprisingly, one often finds experimentally that such reactions, where $A^{\pm}$ is an ionic metal cluster and B a molecular reactant, e.g., N_2 or benzene, occur with a remarkable efficiency.[24−26] In the case of larger transition metal clusters $M_n^{\pm}$ they in fact proceed with nearly collisional rate, which implies that the collision complex must survive many milliseconds, until it can be stabilized by radiation, i.e., by the emission of an IR photon, or by another collision.

Obviously, the experimental observation that a complex between a ligand molecule and a metal atom or cluster does survive implies that the relative kinetic energy of the collision partners, as well as the energy of their binding, cannot remain in the original "collision coordinate", but has to be redistributed between the internal vibrational or possibly also electronic degrees of freedom of the cluster. Only in this way it can avoid dissociating again in a single vibrational period, and survive long enough to be eventually stabilized by an infrared photon emission, or by collision. The formation of a long-lived complex is perhaps not so surprising if one considers that the interaction energy of a metal atom or cluster with an organic ligand may be quite high, in particular if it is charged, and may easily approach 2−3 eV.[18,27,28] For instance, in the $Rh_2(C_6H_6)^+$ complex we find that the binding energy of the benzene ligand exceeds the strength of the metal−metal bond,[25] which was confirmed through calculations by Majumdar et al.[18] The density of states at this internal energy is undoubtedly extremely high, so that once the energy redistribution within the complex by IVR (intramolecular vibrational redistribution) has taken place, the statistical probability of accumulating it again in the dissociation coordinate will be low, and the corresponding lifetime of the complex quite long.

Redistributing this 2−3 eV energy among the internal vibrational degrees of freedom will, in particular in the case of a relatively small cluster, lead to an appreciable increase in the effective temperature of the complex. One might argue that clusters with a limited number of atoms are too small to apply a statistical concept like temperature. However, one can easily calculate an expectation value of the energy of an oscillator at a given temperature. Since a molecule or a cluster contains a known number of oscillators, one can also compute the expectation value of the internal energy as a function of temperature and define the temperature of the complex as the temperature at which the expectation value would be equal to the total internal energy, which, neglecting rotational energy and radiative cooling, is the sum of the original internal energy of the reactants, the binding energy, and the initial kinetic energy in the center of mass frame. Although temperature is a value averaged over a large number of atoms in a macroscopic system, even in the cluster it is possible to average over a number of oscillators. Furthermore, since the energy of the collision complex is undoubtedly well above the limit for IVR, the energy will be efficiently exchanged between the individual vibrational modes—that is what in the first place makes the formation of a long-lived complex in a two-body collision possible. Introducing the concept of such an internal temperature of the metal cluster and of the collision complex is useful, since it allows comparisons of its reactions with bulk chemistry on cold or hot metal surfaces. One might of course talk also about internal energy, but what is important is not the amount of energy per se, but its amount in relation to the size of a given system—in other words the system temperature in the above definition.

The collision of a reactant molecule with an atomic metal ion or with a cluster ion thus results in the formation of a collision complex whose temperature is probably high, but in general unknown, since the exact complex binding energy, the initial temperature of the cluster, and the relative kinetic energy of the reaction partners are either unknown or poorly defined. Discussing and interpreting the metal ion reactions in a mass spectrometer, without taking this temperature rise into consideration, may therefore be meaningless and may easily lead to quite erroneous conclusions and results. In the present paper, we will attempt to illustrate this problem semiquantitatively, based mainly on experimental data of cluster reactions obtained in our laboratory.

To give a more specific example of this effect, one considers a collision of benzene with an M_4^+ ion. The collision complex will consist of 16 atoms and have thus $3N - 6 = 42$ vibrational degrees of freedom. If we assume that the energy to be distributed is about 3 eV or 25 000 cm^{-1}, one gets energies of some 600 cm^{-1} per degree of freedom, corresponding to a "temperature rise" of more than 400 K. This calculation, however, grossly underestimates the actual temperature increase. Most of the internal vibrational frequencies of the benzene molecule, the CH and CC stretching, as well as the CH bending frequencies are far too high to contribute significantly to the "heat capacity" of the cluster at low temperatures. Even the lowest frequency mode, the doubly degenerate e_{2u} benzene ring deformation ν_{20}, is relatively little populated at room temperature. Not considering the zero-point energy, the average internal vibrational energy of a benzene molecule at 300 K is only around 360 cm^{-1}, and even at 1000 K a total energy of only about 8000 cm^{-1} will be stored in the benzene ligand.

A more detailed consideration of the problem, taking into account the known vibrational spectrum of a ligand such as benzene, and employing realistic vibrational frequencies for the metal cluster and for the intercluster modes, suggests that the temperature may actually rise to as much as 2000 K. Vibrational frequencies of metal clusters are usually relatively low, and the cluster itself will thus be the major contributor to the complex heat capacity. The magnitude of the temperature rise will therefore depend on the cluster size and will fall off rapidly with the number of metal atoms in the cluster as its heat capacity increases. Even if initially all the clusters studied had the same low temperature as determined by the cluster source,[29] the effective temperature of the collision complex at which the reaction proceeds will invariably be higher. It will naturally depend on the magnitude of the ligand−cluster binding energy, and in particular it will be steeply dependent upon n, the number of metal atoms in the cluster. This dependence on temperature is then clearly evidenced in the observed reactions, which we will discuss in the following sections.

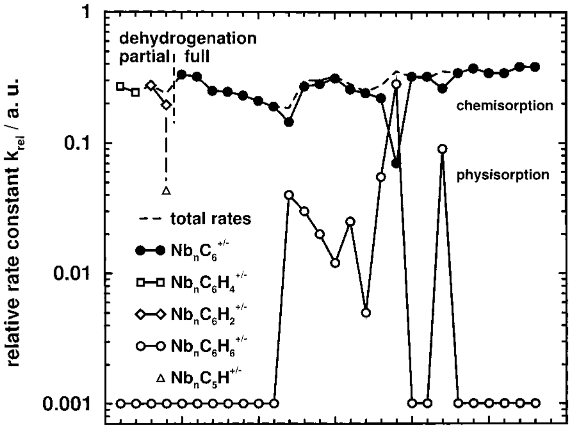

Figure 1. Rate constants for the reaction of cationic niobium clusters, Nb_n^+ with benzene. Solid circles show the rate of the total dehydrogenation reaction, while open circles denote the addition of undecomposed benzene ligand, physisorption. The broken line shows the total rates. Clusters with $n < 5$ only partially dehydrogenate benzene.

3. Study of Nb_n^+ Reactions with Benzene

In the course of the past few years we have employed the FT-ICR technique to explore the chemistry of ionized niobium and other metal clusters, motivated by interesting results on similar systems in fast flow reactors and drift tubes, reported by El-Sayed with co-workers and by several other groups.[30−34] Our studies of the Nb_n^+ cluster reactions with benzene[12] and substituted benzenes[35] in the single-collision regime in the ICR cell have revealed that for most of them the dominant reaction is total dehydrogenation of the hydrocarbon. This is perhaps not surprising, since a simple consideration of the reaction thermochemistry clearly indicates that formation of a metal carbide and of hydrogen is the thermodynamically favored channel. While the enthalpy of formation of benzene is positive, the highly refractory niobium carbide is surely a strongly exothermic product. Little is known about the thermodynamic properties of the niobium carbide itself, but the formation enthalpies of closely related high-melting, interstitial carbides like ZrC, TiC, VC, or TaC are all exothermic by more than 1000 kJ/mol.[36] Combining this with the enthalpy of formation of benzene suggests that the dehydrogenation reaction leading to hydrogen and metal carbide should be strongly exothermic by more than 800 kJ/mol. An independent estimate of the cohesion energy of niobium carbide suggested a value of 607(±7) milli-Rydberg per atom, corresponding to a heat of formation of −796.5(±9) kJ/mol.[37]

Similar arguments should apply for most transition metals, and dehydrogenation with the formation of metal carbide will be strongly thermodynamically favored. When the exothermic dehydrogenation takes place, even more energy is released than in the initial formation of the physisorbed complex, and most of it will again be redistributed in the product “carbide” cluster and will heat it to an even higher temperature, which again for smaller clusters can easily exceed 2000 K. Under these circumstances a complete evaporation of molecular hydrogen may be expected, and this is consistent with the observation that for most niobium clusters complete dehydrogenation of benzene is the dominant reaction, as depicted in Figure 1. One easily understandable exception to this statement is represented by very small Nb_n^+ clusters with $n < 5$ for which one finds both in the case of the reaction with benzene, as well as with several other hydrocarbons, only partial dehydrogenation. For such small clusters with only a few metal atoms the exothermicity of the reaction is undoubtedly smaller, since too few metal−carbon bonds can form, and a stable metal carbide structure can probably not develop.

In spite of this general observation that the larger, $n > 5$, niobium clusters totally dehydrogenate benzene, it was found that several specific sizes behaved anomalously in reactions with benzene. In particular, clusters in the range of $n = 12-19$, as well as $n = 22$, besides fully dehydrogenating benzene, also attach or “physisorb” C_6H_6 molecules without decomposition, even in the nearly collision-free environment of the mass spectrometer. The fact that the ligands in these complexes have not lost their chemical identity can be demonstrated by means of ligand exchange with deuterated benzene, C_6D_6.

$$Nb_nC_6H_6^+ + C_6D_6 \rightarrow Nb_nC_6D_6^+ + C_6H_6$$

This exchange proceeds without any isotopic scrambling, and in no case any formation of isotopically mixed $C_6H_mD_{6-m}$ species could be detected. A similar anomalous behavior in the range of $n = 15-19$, that is, either no or only partial dehydrogenation, was also found in reactions of niobium clusters with toluene or xylenes. As explained above, thermodynamically for all the larger clusters, in which numerous Nb−C bonds can be formed and a carbide structure can develop, the dehydrogenation reaction should be strongly exothermic, and there is no reason to assume that the thermodynamic equilibrium in the intermediate size range would shift in favor of the unreacted complexes.

We have interpreted the observations in terms of a double minimum interaction potential between the cluster and the organic ligand, as shown schematically in Figure 2, which is similar to potentials often used in discussing chemisorption on bulk surfaces. The external, shallower (1.5−3 eV) minimum here corresponds to the “physisorbed”, undecomposed ligand which is π-electron bound to the cluster surface. This weaker bound external minimum is separated by an activation barrier from the much deeper inner “chemisorbed” potential well, which corresponds to the strongly exothermic, intimate chemical reaction of the ligand with the metal. When the molecular reactant impinges upon the surface of a bulk solid metal, the interaction energy is rapidly dissipated in the solid, and propagates rapidly from the adsorption site, leaving the surface temperature unchanged. As discussed above, the situation is quite different for a cluster within the almost collision-free environment. For the “adsorption” of benzene on the surface of the cluster to occur, the kinetic energy of the reactants, as well as the 2−3 eV interaction energy between the ligand and the ionic metal cluster, has to be redistributed within the finite reaction complex, with the IVR populating mainly the low frequency vibrational or “phonon” modes of the transition metal cluster. The resulting temperature rise may or may not be high enough to allow the reaction to proceed further and to overcome the barrier between the shallow outside “physisorbed” minimum

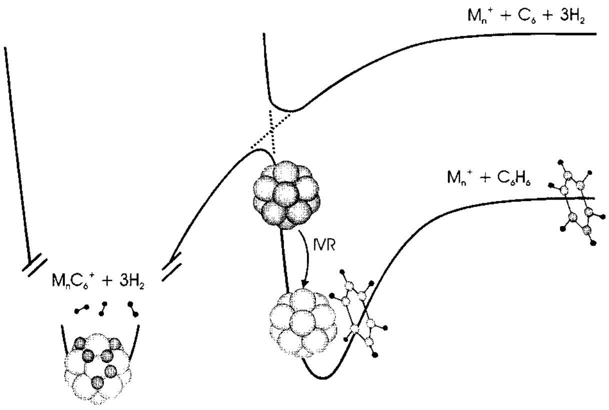

Figure 2. A potential energy diagram showing schematically the double minimum potential for a collision of metal clusters with a molecular ligand, e.g., benzene. Unless either a direct chemical reaction takes place or the complex is stabilized by energy redistribution, IVR, it would redissociate in a single vibrational period. Once IVR has taken place, the energy heats the cluster, and it is lost from the dissociative coordinate. The temperature rise of the metal cluster may then make it possible for the activation barrier to chemical reaction to be surmounted or penetrated: the rate of reaction of the ligand on the hot metal surface is increased. If the reaction occurs, a metal carbide product forms, and molecular hydrogen evaporates from the hot cluster.

and the much deeper chemical well. If the barrier is surmounted, a further strongly exothermic chemical reaction will take place, forming the very stable niobium carbide cluster, and leading to development of an additional large amount of heat, which then results in the evaporation and loss of molecular hydrogen.

The experimental observations suggest that in the case of niobium clusters the barrier heights separating the two minima are in most cases sufficiently low so that the chemical reaction and niobium carbide formation can take place. We suggested that due to some structural property of the clusters, the barriers in the anomalous $n = 12-19$ range and for $n = 22$ are higher, so that the yield of the carbide formation is reduced, and in a part of the cluster–benzene collisions the reaction stops in the outer, "physisorbed" minimum.

4. Secondary Reactions of the Niobium Clusters

The reaction of the metal clusters with benzene does not necessarily stop with the primary step. When allowed to proceed for longer times, collisions with further benzene molecules may take place, and the consecutive reactions that are observed provide further interesting insights. Examination of the secondary reaction step reveals that it is for all the larger niobium clusters ($n > 9$), independent of their size, amazingly simple. Regardless of whether the first step resulted in dehydrogenation or consisted just in adsorption of an undecomposed benzene on the cluster surface, in the second step all hydrogen is lost. For all clusters from $n = 10$ to $n = 27$, the largest size investigated, the unique secondary product is $Nb_nC_{12}^+$. This is exemplified in Figure 3 by the Nb_{19}^+ cluster, for which the anomalous behavior in the first step is most apparent. It is the only cluster for which dehydrogenation to $Nb_{19}C_6^+$ is the minor channel (~20%), and where the formation of the $Nb_{19}C_6H_6^+$ complex is actually the dominant (~80%) reaction. In the reaction with a second benzene molecule, however, both of the benzene ligands are decomposed and all 12 hydrogen atoms are lost, with a unique $Nb_{19}C_{12}^+$ secondary product, presumably a "carbide cluster", being formed:

$$Nb_{19}C_6H_6^+ + C_6H_6 \rightarrow Nb_{19}C_{12}^+ + 6H_2$$

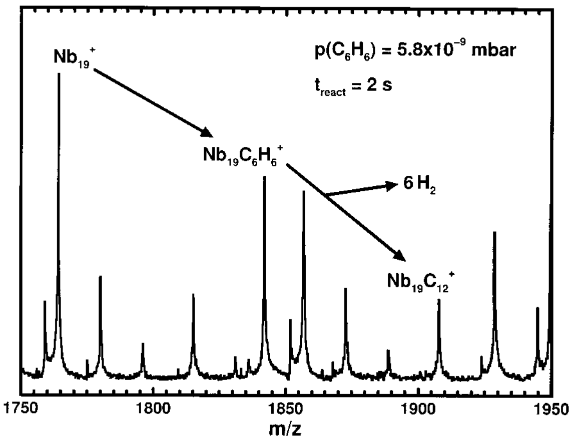

Figure 3. A section of a mass spectrum showing the consecutive reaction of the Nb_{19}^+ niobium cluster cation with two benzene molecules. The dominant first reaction step is addition of an undecomposed benzene, with dehydrogenation being a minor channel. When the $Nb_{19}C_6H_6^+$ primary product collides with a second benzene molecule, its binding energy raises the temperature of the cluster, and allows the system to overcome the activation barrier. A chemical reaction takes place in which both benzene ligands are totally dehydrogenated, a $Nb_{19}C_{12}^+$ carbide cluster forms, and six molecules of H_2 evaporate.

At first sight this result could appear surprising. One might argue that with the adsorption of the first benzene the cluster will be partially coordinatively saturated, the charge more delocalized, and the cluster should become less reactive. The observation suggests exactly the opposite: with the adsorption of the benzene ligand the "reactivity" of the metal appears increased. This result can actually again be very well understood with the help of the above-proposed interpretation, and by the effect of temperature, and of the cluster ion–benzene binding energy. When the first benzene is adsorbed on the cluster, its effective temperature is raised, and as noted above, the rise may or may not be sufficient for the complex to overcome the activation barrier to a chemical reaction. In the case of niobium, this temperature rise is apparently for most clusters adequate to initiate the dehydrogenation reaction, except for some specific cluster sizes where the barrier is higher, and which behave anomalously. For these clusters which form a complex with the first benzene, when the second benzene ligand is attached, its binding energy is again set free, resulting in a further temperature rise. Apparently, within the range of sizes investigated, the amount of energy redistributed in the cluster due to binding two benzene ligands and the corresponding temperature rise are sufficient to overcome the activation barrier, so that the reaction and total dehydrogenation can take place.

5. Ligand Exchange and "Soft Landing" Reactants on Cold Clusters

With the interpretation proposed above, the rise in the temperature of the complex due to the interaction energy between the ligand and the cluster surface is instrumental in overcoming the barrier separating the two potential minima. It would therefore seem that the probability of stabilizing the ligand in the external minimum should be enhanced if one could prepare the complex cold. In several recent studies we have demonstrated that such cold complexes can indeed be prepared and investigated using a simple ligand exchange technique.[22,38] Cold metal clusters solvated by suitable inert ligand molecules or atoms are first produced, which can readily be accomplished by adding for instance argon or xenon atoms to the helium

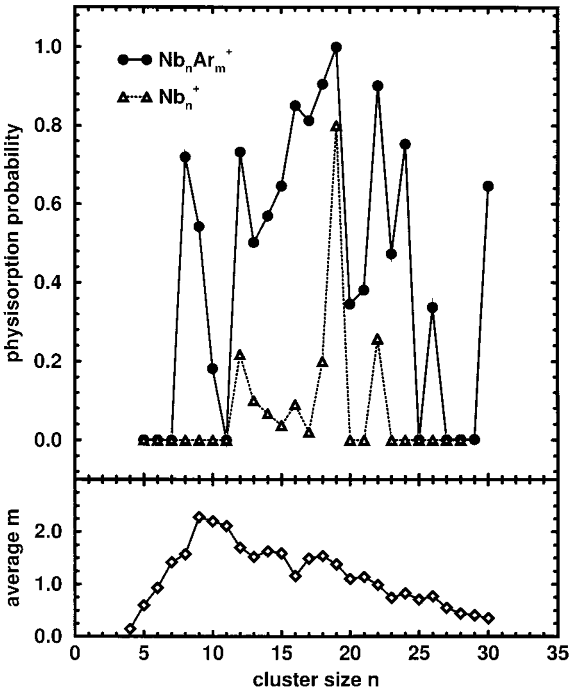

Figure 4. Comparison of the probabilities of adsorbing undecomposed benzene ligands for bare Nb_n^+ niobium cation clusters with $Nb_nAr_m^+$ clusters solvated with m argon atoms, with the bottom plot showing the mean number of argon ligands m as a function of the number of niobium atoms n. For bare clusters (open triangles in the top plot) the addition is only observed for clusters $n = 12-19$ and $n = 22$. When solvated by argon atoms, the probability of physisorbing undecomposed benzene is for most cluster sizes greatly increased. Some clusters, e.g. $n = 5-7$, 11, 25, and 27$-$29 completely dehydrogenate benzene, regardless of the number of argon atoms.

carrier gas flow, or by expanding with pure argon instead of helium. The ionic transition metal$-$rare gas complexes formed in the supersonic expansion laser vaporization source are then transferred into the ICR cell and trapped. The exposure to a reactant gas at the low pressures used in these experiments gave rise to about one collisional encounter per second. Under these conditions the desired ligand, even though in principle reactive, can often be successfully “soft landed” on the cluster without reacting. It is exchanged for one or more of the inert atoms, which evaporate from the complex and carry away the excess interaction energy.

The ligand exchange technique worked very well also with niobium clusters, and simply by substituting argon for the helium as a carrier gas and optimizing slightly the source conditions, niobium clusters solvated by argon, $Nb_nAr_m^+$ could readily be produced. Such an experiment usually produces clusters with a distribution in m, the number of argon atoms. Under conditions used in the present study of niobium cluster ions with benzene, the range was typically $0 \leq m \leq 7$, with an average around $m = 2$. The results of reactions of such argon solvated clusters with benzene are in Figure 4 compared with the reactions of the bare clusters. Here the data points in the top diagram give the fraction of clusters of a given size which add benzene without dehydrogenation, while the plot at the bottom gives the average number of argon ligands. The physisorption probability was determined as the relative intensity of the physisorbed and the sum of the physisorbed and chemisorbed products at a reaction time where the reactant ions are mostly gone. Although among bare clusters denoted by triangles only for $n = 12-19$ and $n = 22$ is addition of benzene observed at all, and only for $n = 19$ this is the dominant process, the probability of stabilizing the complex without dehydrogenation is clearly greatly increased by the argon ligands. As shown by the full circles, with argon ligands “physisorption” becomes the dominant process for many more cluster sizes, and it also occurs for some clusters which without argon ligands only totally dehydrogenated benzene. Removal of the benzene$-$cluster binding energy by the argon atoms decreases significantly the reactivity of the clusters.

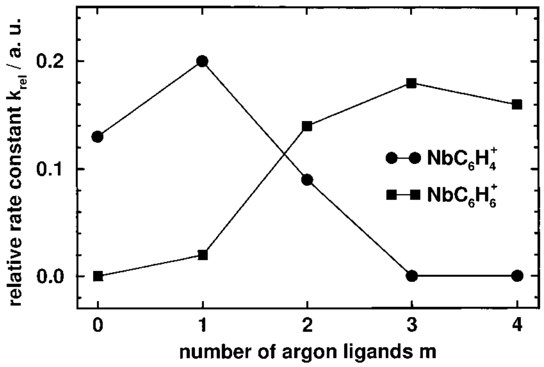

Figure 5. Example of tuning of the reactivity of an ion by the number of inert ligands. Bare Nb^+ dehydrogenates benzene, yielding $NbC_6H_4^+ + H_2$ (circles). The plot shows that for solvated $NbAr_m^+$ ions the probability of dehydrogenation decreases with increasing m, so that for $m > 3$ only addition of benzene (squares) is detected.

The results, however, also indicate that in spite of the efficient cooling, for some values of n even the ligand exchange technique does not prevent benzene decomposition and dehydrogenation. This is apparent in Figure 4 for instance for the $n = 5-7$, $n = 11$, $n = 25$, or $n = 27-29$ species. In these cases, the reaction results exclusively in $Nb_nC_6^+$, regardless of whether the initial metal cluster was bare, or solvated with argon ligands. This apparently again reflects the size-dependent height of the intrinsic activation barrier, and the size specific changes in the cluster structure. If an appreciable barrier is present, one can “tune” the cluster reactivity by controlling its temperature by the argon ligands; if, however, the barrier is either very low or completely absent, then the reaction will proceed even in the cold cluster when its “heating” is prevented by the ligand exchange technique.

Such “tuning” of the reactivity is demonstrated more specifically for the solvated $NbAr_m^+$ ions in Figure 5, which shows the product distribution studied for size-selected clusters as a function of the number of argon ligands m. Bare monatomic Nb^+ partially dehydrogenates benzene, giving a unique $NbC_6H_4^+$ product. For the $m = 1$ ions, the reaction rate increases, since the presence of the argon ligand apparently increases the reaction cross section and facilitates the formation of a longer lived reaction complex. Furthermore, in addition to the dehydrogenated product, one observes also about 10% of complex with benzene with no dehydrogenation. For $m = 2$, the latter process already prevails, and for $m > 3$ no dehydrogenation at all is observed, and the stabilized benzene complex is the only product.

An additional advantage of the ligand exchange technique is that it can be used to generate complexes with ligands which are difficult to stabilize and do not readily react with the metal clusters under single collision conditions in high vacuum. As discussed above, benzene, as well as ethylene, acetylene, and many other unsaturated hydrocarbons readily form complexes, or react chemically with the transition metal clusters. This is, however, not the case with methane and other small alkanes, where as a rule under similar conditions no reactions with the bare metal clusters are observed. On the other hand, by exchanging the unreactive methane or other alkanes for still more weakly bound inert ligands, for instance argon, their complexes with the metal clusters can easily be produced and stabilized. As a consequence, exactly the opposite effect as discussed above for the reaction with benzene can be accomplished, and reactions that are not observed with bare clusters may occur.

As an example we have investigated the reactions of rhodium clusters with methane. Previous studies of the reaction of monatomic Rh^+ have shown that its reaction with methane is endothermic,[17,38] and under thermal conditions none is observed. When a distribution of bare Rh_n^+ clusters with $n = 1-10$ is examined, one finds again that most of them do not react with methane, and also no "physisorbed" complexes are formed. An exception here is the cationic dimer, which partially dehydrogenates methane and forms the $Rh_2CH_2^+$ product. The main reason for this drastically reduced reactivity and complex formation efficiency for methane and other small alkanes is the much lower cluster ion−methane binding energy. The much lower total internal energy available in the collision complex implies a much lower density of accessible states, and makes the occurrence of IVR and stabilization of the complex by the statistical energy redistribution within the cluster on the time scale of a single gas-phase collision much less probable and efficient.[39]

If, on the other hand, one uses metal clusters solvated with argon, $Rh_nAr_m^+$, one observes that not only are complexes with methane $Rh_n(CH_4)_m^+$ readily produced for all cluster sizes n,[40] but also in addition to the $n = 2$ cluster, also Rh_3^+ now chemically reacts with methane, forming a dehydrogenated $Rh_nCH_2^+$ product. This observation resembles reactions in low-temperature matrices[41] in that by stabilizing a long-lived complex, one ensures a "sustained proximity" of the two reactants, the metal cluster and the methane. Under these circumstances even a reaction which is too slow to occur with any efficiency on a time scale of a gas-phase collision may become observable.

For $n = 4$ and still larger n values, one can readily form complexes with one or more methane ligands, but no dehydrogenation is detected. This could be due to a number of different reasons. Similar to the reactions with benzene it could reflect the reduced effective temperature due to the increased size of the system over which the binding energy is redistributed. The most likely interpretation is, however, an increased height of the activation barrier for the dehydrogenation reaction, perhaps due to the possibility of delocalizing the positive charge over a larger metal cluster. If this barrier is sufficiently high, no observable reaction may occur even on the relatively long time scale of the ICR experiment. Last, but not least, it cannot be excluded that the overall thermochemistry may change again, and formation of $Rh_nCH_2^+$ may become endothermic for $n >$ 3. It is highly desirable that this be examined by suitable calculations or guided ion beam studies.

6. Rhodium Cluster Reactions with Benzene

Another system we have previously investigated in some detail is the reactions of ionic rhodium clusters with benzene. We have now extended the Rh_n^+ cluster studies to larger values of n, and also reexamined our older data for secondary reactions. Our earlier studies of rhodium reactions which are summarized in Figure 6 have shown that in particular smaller clusters have a somewhat lower tendency toward totally dehydrogenating benzene and other hydrocarbons than niobium clusters of the same size.[25,26] This observation is consistent with the known chemical properties of the elements: rhodium is somewhat less reactive toward carbon than niobium, and on the other hand, somewhat more reactive toward hydrogen.

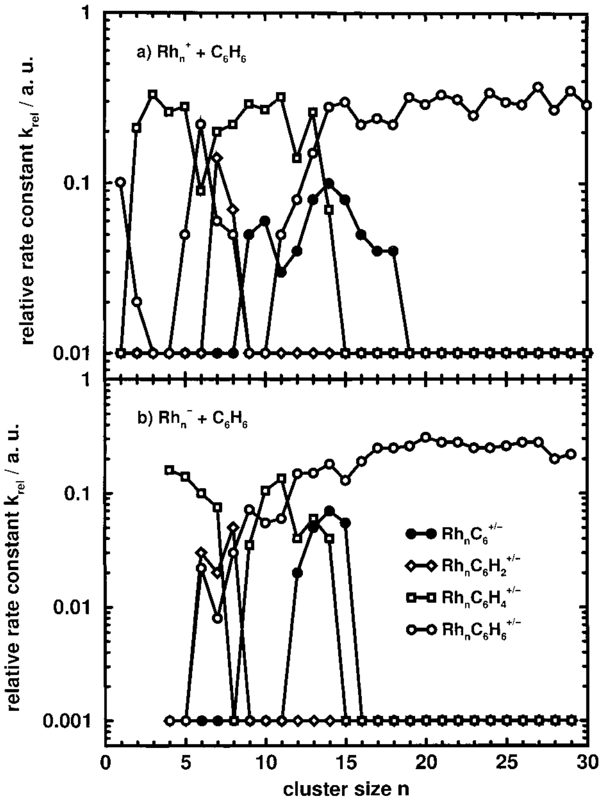

Figure 6. Relative rate constants for the reactions of Rh_n^+, $n = 4-30$, cluster cations (a) and anions (b) with benzene. The degree of dehydrogenation increases while the overall yield of dehydrogenation reactions decreases with cluster size. Cation clusters $n \geq 19$ and anion clusters $n \geq 16$ only physisorb undecomposed benzene with no hydrogen loss.

Small clusters were found to dehydrogenate benzene only partially, with the degree of dehydrogenation increasing, but the overall reactivity decreasing with the size of the cluster. As can be seen in Figure 6a, total dehydrogenation of benzene is observed for clusters with $n = 9-18$, but with increasing cluster size there is also an increased competition of "physisorption" of undecomposed benzene. This process in fact begins to dominate for all clusters with $n > 13$, and for $n > 18$ it becomes the only observed process. All clusters from $n = 19$ up to the largest sizes studied of about $n = 40$ only add undecomposed benzene without any hydrogen loss.

These observations are again nicely consistent with the effect of cluster temperatures. The binding energy between the benzene and the cluster "surface", that is the amount of energy which has to be redistributed within the cluster as the complex forms, can to a first approximation be considered independent of the cluster size. On the other hand, the heat capacity of the cluster will increase, and the temperature rise will correspondingly decrease with the cluster size. Apparently for clusters with $n \geq 19$ the increase in the effective temperature is not enough to surmount the activation barrier, and the benzene is simply attached to the surface without reacting further.

Interesting insight is provided again by secondary reactions with additional benzene molecules. When one now examines the reaction of rhodium clusters with a second benzene molecule, one finds out that most of the $n \geq 19$ species which only added an unreacted benzene ligand in the first step dehydrogenate the second benzene ligand:

$$Rh_nC_6H_6^+ + C_6H_6 \rightarrow Rh_nC_{12}H_6^+ + 3H_2$$

Again, the binding energy of the second ligand further increases the temperature of the complex and allows the activation barrier to be surmounted and the dehydrogenation to take place. Interestingly, in contrast with the niobium clusters where in the second reaction step both benzene ligands were decomposed and all hydrogen lost, in the rhodium case only one of the benzene molecules appears to be dehydrogenated, resulting in a product with 12 carbon and six hydrogen atoms. While we believe that the product may be a $Rh_nC_6^+$ cluster with one benzene ligand attached, we have not investigated this product further, and the mass spectrum alone naturally does not give any indication of its structure.

Clearly, the major causes of the less complete dehydrogenation in the case of rhodium clusters are again the above-mentioned differences in the chemical properties between the two elements, and the resulting lower exothermicity of the dehydrogenation reactions in the rhodium case. Apparently the three escaping hydrogen molecules can remove enough energy from the complex to prevent the dehydrogenation of the second benzene ligand. It may be noted here that one could imagine that the dehydrogenation of the benzene molecule in the second reaction step might provide enough energy to also evaporate the second benzene ligand:

$$Rh_nC_6H_6^+ + C_6H_6 \rightarrow Rh_nC_6^+ + C_6H_6 + 3H_2$$

Such a formation of the $Rh_nC_6^+$ carbide cluster as a secondary reaction product was, however, not detected. Further experiments would be needed to firmly establish the reaction mechanisms and confirm the structures of the secondary reaction products.

7. Reactions of Anionic Clusters

One of the drawbacks of FT-ICR studies is that the investigated clusters are ionic, and it is therefore difficult to establish which reactions reflect the intrinsic properties of the metal and which are the consequence of the ionic nature of the reacting cluster. One can, of course, study and compare the reactions of cations and neutrals, for instance in flow reactors of various designs, but the interpretation of such experiments is made difficult by the necessity to subsequently ionize the neutral products prior to detection.[30,32,33,42] The FT-ICR studies can unfortunately not be easily extended to neutral species. With our experimental setup, however, it is easily feasible to examine reactions of the corresponding cluster anions. Should one find that the reactions of the anions are entirely different from those of the cations, it might be difficult to draw conclusions about the reactions of neutral metal clusters. If, on the other hand, one finds that both the anions and cations react in essentially the same way, it becomes quite reasonable to attribute the observed chemistry to the intrinsic properties of the metal, rather than to the ionic nature of the cluster. We have therefore reinvestigated, both in the case of rhodium and niobium, also the reactions of the anionic clusters.[26] The conclusion in both cases was that the reactions of anions and cations are remarkably similar, and in each case the similarities and differences provided additional interesting insights.

Two interesting observations can be made and two different ideas inferred from the comparison of anionic and cationic niobium clusters. As noted above, depending on the cluster size the first reaction step may involve simple addition of an undecomposed benzene ligand, or its total dehydrogenation, with for small clusters $n < 5$ also partial dehydrogenation being observed. When one adds all the observed reaction channels, and examines the overall reaction rate as a function of cluster size n, one finds that for the cations this is almost flat, as can be seen in Figure 7a. A more quantitative evaluation suggests that the reaction probability for cations in the entire range from $n = 1$ to $n = 30$ is close to unity; that is, it is controlled by the collision rate. For the anions, Figure 7b, the situation is quite different, with the smallest species studied, $n = 3$ and 4, reacting under otherwise identical conditions almost 2 orders of magnitude slower. The reaction efficiency, however, increases rapidly as a function of n, so that above $n \sim 25$ the rates of anions and cations appear essentially indistinguishable, both occurring with collision rate.

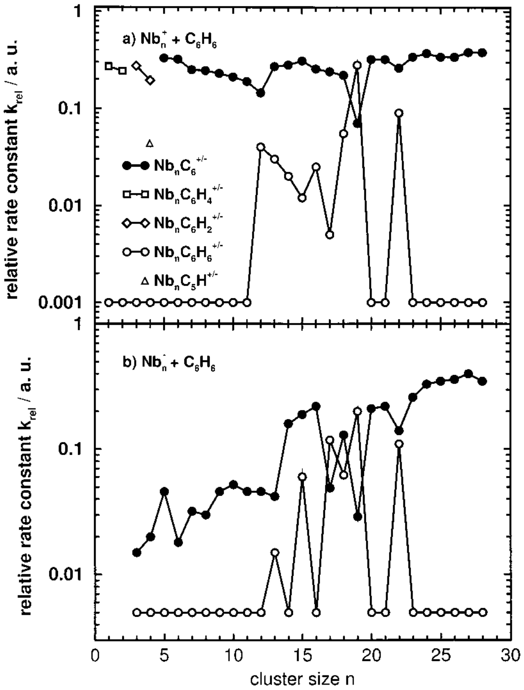

Figure 7. Comparison of the rates of reactions of niobium cluster cations, Nb_n^+ (a), and anions, Nb_n^- (b), with benzene. The reaction rates as a function of size are relatively flat for cations, but rise steeply with n for anions, with the small anions being unreactive. On the other hand, there are similar specific reactivity patterns, and in particular for both anions and cations the $n = 19$ and $n = 22$ cluster sizes show a particular propensity for physisorbing benzene without decomposition and hydrogen loss.

We suggest that this reflects the dependence of the first reaction step—that is, formation of a long-lived π-bonded cluster−benzene complex—on the cluster charge. For the small clusters, the negative charge, mainly distributed on the surface of the cluster, presumably hinders attachment of the benzene ligand. As the cluster size increases, the negative charge becomes progressively more delocalized, so that for $n > 25$ the effect becomes negligible. We also propose that from these results one can infer that at least for the larger clusters the charge is unimportant and that if one could under similar conditions study the reactions of neutral clusters, similar overall reaction rates would be observed.

A second interesting point resulting from the niobium anion−cation−cluster comparison involves the anomalous reactions of some particular cluster sizes. As noted above, specifically the $n = 19$ and $n = 22$ species react differently than the neighboring cluster sizes in that they preferentially add undecomposed benzene, and the dehydrogenation reaction is suppressed. The main, and perhaps at first surprising, result of the anion study was the observation that the anions behave almost identically, and exactly the same cluster anion sizes, that is, $n = 19$ and $n = 22$, again display lower reactivity, and higher propensity toward the attachment of undecomposed benzene. The anomalous behavior and stability of specific sizes of alkali metal clusters was often successfully interpreted in terms of an electronic "jellium" model,[43−46] with these particularly stable "magic" clusters being determined by the numbers of valence electrons which lead to closed electronic shells in this, basically a particle in a spherical box, model. The fact that in the present case the same cluster sizes of cations and anions exhibit essentially the same reactivity patterns suggests strongly that the geometries of these clusters, rather than details of their electronic structure, are responsible for their anomalous behavior. Again, the identical behavior of anions and cations indicates that also the corresponding neutrals would behave similarly; that is, we predict that also neutral $n = 19$ and $n = 22$ clusters will preferentially add or "physisorb" undecomposed benzene ligands.

As noted above, the chemistry of rhodium clusters is different from that of niobium, and again new interesting conclusions can be inferred from the rhodium cation−anion cluster comparison. For the cations shown in Figure 6a, the main conclusion was that while the *degree* of dehydrogenation increases with the cluster size, its overall *rate* decreases. As one proceeds from small to large clusters, the first region characterized by a loss of a single H_2 molecule is followed by a region with a preferential $2H_2$ loss, and eventually a total dehydrogenation, that is, loss of $3H_2$, is observed. Concurrently with the dehydrogenation reactions, also adsorption of an undecomposed benzene ligand is observed, with the importance of the latter process increasing with the cluster size. It becomes the dominant process starting with $n = 15$, and is the only reaction observed for $n \geq 19$. These results are again in perfect agreement with the proposed effects of the size-dependent cluster heating. For species with more than 19 atoms, the energy dissipated within the collision complex by the benzene ligand adsorption is no longer sufficient to raise the temperature of the large clusters above the threshold for thermal activation of the dehydrogenation reaction.

The anions, whose reactions are summarized in Figure 6b, behave almost identically, except that the sizes at which the changes in the dehydrogenation behavior occur are all shifted toward smaller values of n. Thus, the "physisorption" becomes for anions the dominant process for $n = 11$ rather than 15, and already above $n = 16$, rather then 19, no dehydrogenation is detected. The interpretation is again connected with the effect of charge already discussed for the niobium clusters. The presence of the delocalized negative charge on the surface reduces for small clusters the binding energy of the ligand, and thus also the amount of energy which is dissipated in the cluster. Assuming that the charge has little influence upon the heat capacity of the cluster, the overall temperature rise associated with the attachment of the benzene ligand will be smaller for the anionic clusters.

8. Reactions of Atomic and Small Molecular Ions

The above conclusions derived from our cluster studies are readily applicable to a variety of phenomena in gas-phase reactions of atomic and small molecular ions. It is quite important to point out the difference between gas-phase single collision reactions, and reactions at high pressure or in the condensed phase. For a gas-phase reaction any barriers between the reactants and products, whose energies are lower than the total energy in the system, can of course affect the branching ratios, but the reaction will in general proceed toward the products. In a condensed phase system, on the other hand, such barriers may be extremely important, and if they are high, the reaction is quite likely not to reach the final product but to stop in the interceding minima.

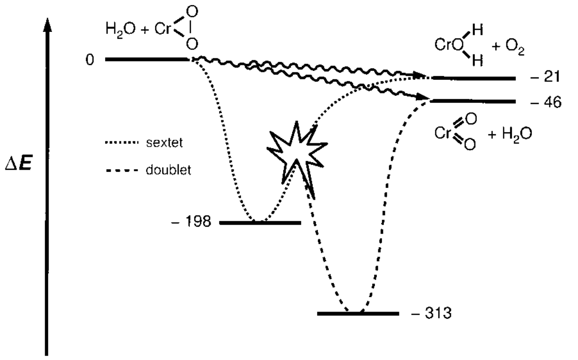

Figure 8. A schematic drawing of the potentials involved in the $[Cr,O_2]^+ + H_2O$ system, explaining the efficient conversion of the chromium dioxygen complex cation $Cr(O_2)^+$ into the chromyl cation CrO_2^+ upon collisions with water. The sinuous lines indicate, similar to a Feynman graph in particle physics, that the highly excited and rapidly isomerizing $[Cr,O_3,H_2]^+$ complex is floating above the features of the potential energy surface, eventually proceeding to the products. Approximate relative energies based on B3LYP/6-311G(3df,3pd) computations are given in kJ/mol.

The collision complex binding energy may in fact be crucial for the high reactivity of bare transition metal ions, which is usually ascribed primarily to the absence of coordinative saturation.[17] Conversely, a reaction intermediate can be "frozen" if the binding energy of the collision complex is removed in a ligand exchange reaction, essentially mimicking a three-body collision. We have recently demonstrated that the platinum hydridomethyl complex, which is the global minimum of the $[Pt,C,H_4]^+$ potential energy surface and an intermediate of the reaction $Pt^+ + CH_4 \rightarrow PtCH_2^+ + H_2$, can be stabilized and the dehydrogenation reaction be blocked if the reaction is done with $PtAr_n^+$ instead of bare Pt^+.[22] By choosing the right number of argon ligands, one can switch the dehydrogenation reaction on and off, which can be seen as a gas-phase equivalent to the temperature-controlled selectivity of an industrial catalyst.

Another regularly observed feature is the reactivity increasing with the size of the neutral reactant molecule. Cornehl et al.[47] reported that the lanthanide cations La^+, Ce^+, and Gd^+ dehydrogenate alkanes larger than ethane, and the reaction rate increases with increasing polarizability. The binding energy of the weakly bound collision complex, however, also increases with the polarizability of the prospective ligand, and more energy is available in the complex for promoting the dehydrogenation reaction. This effect is amplified by the prolonged lifetime of the collision complex with increasing reactant size, as was recently shown by Janaway and Brauman,[48] and by possible changes in the overall thermochemistry of the reaction. Partially dehydrogenated alkanes may act as chelating ligands, and increase the ligand binding energy with increasing size of the alkane.

The heated collision complex may also come into play in the collisional cooling of ions. It is a fairly common practice in FT-ICR experiments to cool the ions of interest collisionally before the mass selection. After this procedure the ions are thermalized, and the experiment is done at thermal energies. While this routinely applied procedure is useful and indeed results in ions which are translationally and vibrationally cooled to ambient temperature, based on the above conclusions we believe that speaking of thermal collisions may at times be misleading. Thermal conditions seemingly imply that, e.g., isomerization reactions that require significantly more than thermal energy, i.e., $kT = 25$ meV or 2.5 kJ/mol, do not readily occur. The binding energy of a typical, so-called inert collision gas like argon, to a transition metal cation can be up to 50 kJ/mol[49,50] or 20 times more than thermal energy. The most common impurity in UVH environments, H_2O, with a large permanent dipole, exhibits bond energies of up to 180 kJ/mol to the first-row transition metal ions.[51] These binding energies, redistributed in a small molecular ion, can amount to vibrational temperatures of several thousand kelvin, which illustrates that a typical collision complex is indeed far away from thermal conditions. Rather than cooling the ions, the collision gas may in fact cause their annealing, and certain higher energetic isomers may be lost.

We have recently demonstrated that this effect can have a serious impact on FT-ICR studies of metal complexes in our study of the Cr^+, O_2, H_2O system,[52] with its potential energy diagram shown schematically in Figure 8. The cationic chromium dioxygen complex $Cr(O_2)^+$ can be selectively produced in a laser vaporization source by adding traces of oxygen to the helium carrier gas. This ion undergoes an efficient isomerization reaction upon collisions with H_2O or CO, resulting in the chromyl cation, CrO_2^+. Again, the $[Cr(O_2),H_2O]^+$ collision complex contains the 1−1.5 eV binding energy, which when redistributed by IVR among the complex vibrations, becomes readily available for isomerization reactions involving multiple curve crossings. The situation is conceptually similar to a reaction in particle physics, where the details of the reaction remain obscured, while it is well-known that the "collision complex" is highly excited. This is reflected in the Feynman graphs, where the ill-described collision complex is represented by a sinuous line. Similarly, the sinuous lines in Figure 8 indicate that the highly excited $[Cr(O_2),H_2O]^+$ is "floating" above the features of the potential energy surface. Especially the location of the two curve crossings from the sextet via the quartet to the doublet surface remains unknown, as indicated by the hollow star in the middle. As long as the region where the curve crossings occur lies well below the floating lines, their exact location is essentially irrelevant.

9. Summary

One frequently employs mass spectroscopic studies of the reactions of metal atoms, ions, and clusters as model systems for catalytic processes on metal surfaces. When one tries to transfer conclusions from such high-vacuum studies to condensed phase systems, one has to carefully consider the differences between the two processes. While reactions on the surface of bulk metal proceed in general under well-defined and experimentally easily measurable temperature and other conditions, in the process of formation of a collision complex in high vacuum a large amount of heat is liberated. When the complex is stabilized, this binding energy between the metal atom or cluster and its reaction partner, e.g., 2−3 eV for benzene, is redistributed in the cluster, raising its temperature. The temperature rise will naturally be inversely proportional to the complex heat capacity, which in turn is proportional to the cluster size n. In the present paper we show that these effects are easily observable in studies of size-selected anionic and cationic metal clusters. If one wishes to draw meaningful conclusions about condensed phase or high-pressure systems from high-vacuum studies, these thermal effects have to be carefully taken into consideration. Conversely, one can experimentally reduce or eliminate the effect of such a temperature rise by a ligand exchange technique, in which the reactive molecule is "soft landed" on cold clusters solvated by inert ligands, such as argon or xenon atoms.

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References and Notes

(1) Marshall, A. G.; Verdun, F. R. *Fourier Transforms in NMR, Optical, and Mass Spectrometry*; Elsevier: Amsterdam, 1990.

(2) Marshall, A. G.; Hendrickson, C. L.; Jackson, G. S. *Mass Spectrom. Rev.* **1998**, *17*, 1.

(3) Reents, W. D.; Bondybey, V. E. *Chem. Phys. Lett.* **1986**, *125*, 324.

(4) Mandich, M. L.; Bondybey, V. E.; Reents, W. D., Jr. *J. Chem. Phys.* **1987**, *86*, 4245.

(5) Maruyama, S.; Anderson, L. R.; Smalley, R. E. *Rev. Sci. Instrum.* **1990**, *61*, 3686.

(6) Elkind, J. L.; Weiss, F. D.; Alford, J. M.; Laaksonen, R. T.; Smalley, R. E. *J. Chem. Phys.* **1988**, *88*, 5215.

(7) Irion, M. P.; Selinger, A.; Wendel, R. *Int. J. Mass Spectrom. Ion Processes* **1990**, *96*, 27.

(8) Mandich, M. L.; Reents, W. D., Jr.; Bondybey, V. E. In *Main Group Clusters: A Review in Atomic Molecular Clusters*; Bernstein, E. R., Ed.; Elsevier: Amsterdam, 1990; p 69.

(9) Schnabel, P.; Irion, M. P.; Weil, K. G. *J. Phys. Chem.* **1991**, *95*, 9688.

(10) Hasse, H.-U.; Becker, S.; Dietrich, G.; Klisch, N.; Kluge, H.-J.; Lindinger, M.; Lützenkirchen, K.; Schweikhard, L.; Ziegler, J. *Int. J. Mass Spectrom. Ion Processes* **1994**, *132*, 181.

(11) Sharpe, P.; Campbell, J. M.; Cassady, C. J. *Organometallics* **1994**, *13*, 3077.

(12) Berg, C.; Schindler, T.; Niedner-Schatteburg, G.; Bondybey, V. E. *J. Chem. Phys.* **1995**, *102*, 4870.

(13) Vakhtin, A. B.; Sugawara, K. *J. Chem. Phys.* **1999**, *111*, 10859.

(14) Schindler, T.; Berg, C.; Niedner-Schatteburg, G.; Bondybey, V. *Ber. Bunsen Ges. Phys. Chem.* **1992**, *96*, 1114.

(15) *Handbook of Heterogeneous Catalysis*; Ertl, G., Knözinger, H., Weitkamp, J., Eds.; VCH: Weinheim, 1997; Vol. 1−5, p 2469.

(16) Somorjai, G. A. *Introduction to surface chemistry and catalysis*; Wiley: New York, 1994.

(17) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121.

(18) Majumdar, D.; Roszak, S.; Balasubramanian, K. *J. Chem. Phys.* **1997**, *107*, 408.

(19) Pavlov, M.; Blomberg, M. R. A.; Siegbahn, P. E. M.; Wesendrup, R.; Heinemann, C.; Schwarz, H. *J. Phys. Chem. A* **1997**, *101*, 1567.

(20) Buker, H. H.; Maitre, P.; Ohanessian, G. *J. Phys. Chem. A* **1997**, *101*, 3966.

(21) Andrews, L.; Zhou, M. F.; Chertihin, G. V.; Bauschlicher, C. W. *J. Phys. Chem. A* **1999**, *103*, 6525.

(22) Achatz, U.; Beyer, M.; Joos, S.; Fox, B. S.; Niedner-Schatteburg, G.; Bonybey, V. E. *J. Phys. Chem. A* **1999**, *103*, 8200.

(23) Achatz, U.; Niedner-Schatteburg, G.; Bondybey, V. E. Manuscript in preparation.

(24) Yin, W. W.; Marshall, A. G.; Marcalo, J.; Dematos, A. P. *J. Am. Chem. Soc.* **1994**, *116*, 8666.

(25) Berg, C.; Beyer, M.; Schindler, T.; Niedner-Schatteburg, G.; Bondybey, V. E. *J. Chem. Phys.* **1996**, *104*, 7940.

(26) Berg, C.; Beyer, M.; Achatz, U.; Joos, S.; Niedner-Schatteburg, G.; Bondybey, V. E. *J. Chem. Phys.* **1998**, *108*, 5398.

(27) Meyer, F., Khan, F. A., Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 9740.

(28) Roszak, S., Majumdara, D., Balasubramanian, K. *J. Phys. Chem. A* **1999**, *103*, 5801.

(29) Labastie, P.; Lhermite, J. M.; Poncharal, P.; Rakotoairsoa, L.; Sence, M. *Z. Phys. D Atom. Mol. Cl.* **1995**, *34*, 135.

(30) St. Pierre, R. J.; El-Sayed, M. A. *J. Phys. Chem.* **1987**, *91*, 763.

(31) St. Pierre, R. J.; Chronister, E. L.; Song, L.; El-Sayed, M. A. *J. Phys. Chem.* **1987**, *91*, 4648.

(32) St. Pierre, R. J.; Chronister, E. L.; El-Sayed, M. A. *J. Phys. Chem.* **1987**, *91*, 5228.

(33) Zakin, M. R.; Cox, D. M.; Kaldor, A. *J. Phys. Chem.* **1987**, *91*, 5224.

(34) Bowers, M. T.; Kemper, P. R.; Helden, G. v.; Hsu, M. T. In *Fundamentals of Gas-Phase Ion Chemistry*; Jennings, K. R., Ed.; Kluwer Academic: London, 1991.

(35) Berg, C.; Schindler, T.; Lammers, A.; Niedner-Schatteburg, G.; Bondybey, V. E. *J. Phys. Chem.* **1995**, *99*, 15497.

(36) Mallard, W. G., Ed. *NIST Standard Reference Database Number 69*, February 2000 Release; http://webbook.nist.gov.

(37) Guillermet, A. F.; Häglund, J.; Grimvall, G. *Phys. Rev. B* **1992**, *45*, 11557.

(38) Chen, Y. M.; Armentrout, P. B. *J. Phys. Chem.* **1995**, *99*, 10775.

(39) Bondybey, V. E. *Annu. Rev. Phys. Chem.* **1984**, *35*, 591.

(40) Albert, G.; Berg, C.; Beyer, M.; Achatz, U.; Joos, S.; Niedner-Schatteburg, G., Bondybey, V. E. *Chem. Phys. Lett.* **1997**, *268*, 235.

(41) Frei H.; Pimentel, G. C. In *Chemistry and Physics of Matrix Isolated Species*; Andrews, L., Moskovits, M., Eds.; North-Holland: New York, 1989.

(42) El-Sayed, M. A. *J. Phys. Chem.* **1991**, *95*, 3898.

(43) Knight, W. D.; Clemenger, K.; deHeer, W. A.; Saunders, W. A.; Chou, M. Y.; Cohen, M. L. *Phys. Rev. Lett.* **1984**, *52*, 2141.

(44) Cohen, M. L.; Chou, M. Y.; Knight, W. D.; de Heer, W. A. *J. Phys. Chem* **1987**, *91*, 3141.

(45) Eckhardt, W. *Phys. Rev. A* **1984**, *29*, 1991.

(46) Jarrold, M. F. In *Clusters of Atoms and Molecules*: *Theory, Experiment*; Haberland, H., Ed.; Springer-Verlag: Berlin, 1994; p 418.

(47) Cornehl, H. H.; Heinemann, C.; Schröder, D.; Schwarz, H. *Organometallics* **1995**, *14*, 992.

(48) Janaway, G. A.; Brauman, J. I. *J. Phys. Chem. A* **2000**, *104*, 1117.

(49) Partridge, H.; Bauschlicher, C. W.; Langhoff, S. R. *J. Phys. Chem.* **1992**, *96*, 5350.

(50) Lessen, D.; Brucat, P. J. *Chem. Phys. Lett.* **1988**, *152*, 474.

(51) Dalleska, N. F.; Honma, K.; Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 3519.

(52) Beyer, M. K.; Berg, C. B.; Achatz, U.; Joos, S.; Niedner-Schatteburg, G.; Bondybey, V. E. *Molec. Phys.*, in print.