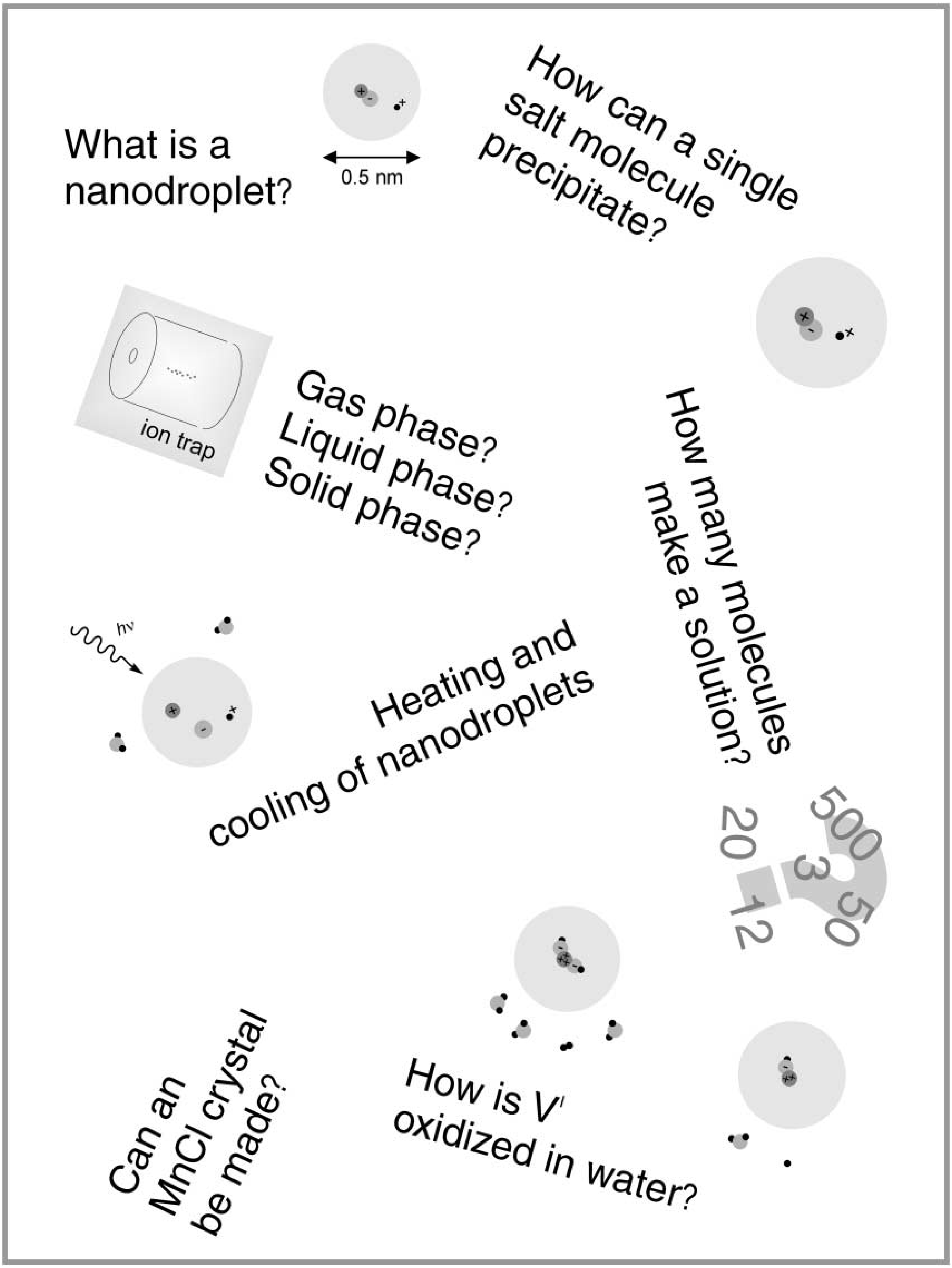
What is a nanodroplet?
0.5 nm
How can a single salt molecule precipitate?
ion trap
Gas phase?
Liquid phase?
Solid phase?
How many molecules make a solution?
hν
Heating and cooling of nanodroplets
500
20
3
50
1
2
Can an MnCl crystal be made?
How is V^I oxidized in water?

Aqueous Chemistry of Transition Metals in Oxidation State (I) in Nanodroplets

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Abstract: "Nanodroplets" consisting of a central ion surrounded by a solvation shell of water molecules provide an interesting medium for studies of aqueous transition-metal chemistry in the unusual oxidation state (I). While V^I undergoes efficient, solvent shell dependent redox reactions to V^{II} and V^{III}, the absence of any similar reactivity in aqueous Cr^I, Mn^I, Fe^I, Co^I, Ni^I, and Cu^I clusters is explained by a rapid precipitation of the corresponding single monochloride molecules from the nanosolutions.

Keywords: electrochemistry · hydrates · gas-phase reactions · mass spectrometry · redox chemistry

Introduction

Transition metals are important in industry and technology, and their chemistry is of an appreciable interest. The ease with which they form complexes makes them useful homogeneous catalysts in a variety of reactions involving ligand exchange. The available d electrons allow most of these elements to occur in a variety of oxidation states, and unlike main group elements, whose oxidation numbers usually change in increments of two, the same transition metal often forms stable compounds adopting both even and odd oxidation numbers.

Interestingly, the oxidation number one is quite uncommon in transition-metal compounds.[1] This is the consequence of the preferred $(n-1)d^m ns^2$ ground state electronic configuration of the metal atoms, with two available valence shell s electrons. Somewhat exceptional in this respect are the coinage metals, which due to the stability of a closed d^{10} electron shell also exhibit a low energy $(n-1)d^{10}ns$ electron configuration, and may occur as monovalent. For most of the other transition metals, the M^+ ions in aqueous solutions are not known; this is usually attributed to efficient disproportionation reactions. In spite of the relatively high second-ionization potentials, the disproportionation is exothermic due to the high hydration energies of multiply charged cations. Even the Cu^+ ions in solutions readily disproportionate, $2Cu^+ \rightarrow Cu + Cu^{2+}$, unless stabilized by the formation of strong complexes, or in highly insoluble compounds. Oxidation of the transition metal(I) ions in solution is promoted by the presence of other ions, for instance H^+ or OH^-.

Ions solvated by a finite number of ligand molecules can provide a very useful and attractive gas-phase system for solvation studies.[2] Such $X^{\pm}(H_2O)_n$ ions, in which X can be almost any element and in which the number of water molecules n may range from zero to more than 100, can be easily prepared by modern methods. In the case of transition metals, the decay mechanisms from bulk solution are often not operative in the cluster, since disproportionation is not feasible if only one ion is present and hydronium or hydroxide ions are not available in the small cluster. The method used in our laboratory to produce the solvated ions is laser vaporization of a suitable solid target followed by a supersonic expansion in a helium/water mixture.[2b, 3a] The finite ionic clusters produced in this way then represent well-defined "reactors", in which additional gaseous species can be "dissolved" and in which a wide range of processes and reactions can be studied.[2a,b] This concept article reviews several recent studies of such clusters, which focused in particular on transition metal chemistry,[4, 5] and discusses their implications for redox reactions and electrochemistry.

Nanosolutions in a Collision-Free Environment

Figure 1 illustrates the basic principle of our experiment.[2a,b, 3] A laser pulse of typically 5 mJ energy and of about 5 ns duration hits a solid metal target and produces hot, partially ionized, metal vapor. An accurately timed gas pulse of a helium/water mixture dilutes and cools the metal plasma and carries it down the flow channel towards an expansion nozzle. Water clusters form in the gas pulse and during the expansion,

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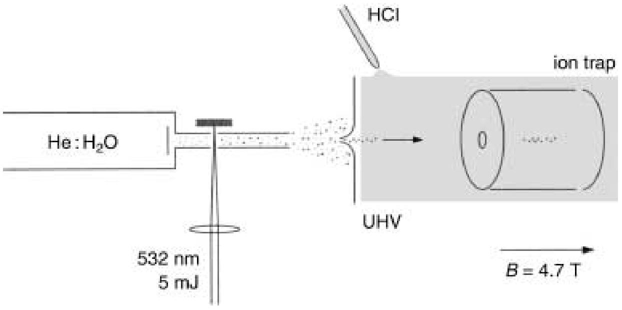

Figure 1. Nanodroplets are formed by a pulsed supersonic expansion of helium–water mixtures doped with metal ions, produced by pulsed laser vaporization of the solid metals. The resulting nanosolutions, which consist of a single ion in 5–100 water molecules, correspond to a 10–0.5 M concentration. The ionic clusters are transferred to the penning ion trap of the Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer, where they are stored under ultra high vacuum. In the absence of collisions, the nanodroplets interact solely with ambient black-body radiation. Optionally a reaction gas, for example, HCl, can be introduced at a constant backing pressure. To monitor the reaction, ultra-high resolution mass spectra are taken as a function of trapping time.

and solvate the individual singly-charged metal ions. The source parameters can be adjusted to produce cluster-ion distributions consisting almost exclusively of $M(H_2O)_n{}^+$ species. The ions leaving the source are transferred to the cell of the Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer by a system of electrostatic lenses, where they can be stored in the electromagnetic ion trap at a pressure of 10^{-10} mbar. Crucial for the discussed experiments is the timescale and the pressure. In principle, ions can be stored indefinitely in the ICR cell, with the trapping times in typical experiment being 100 ms up to 100 s. At the residual gas base pressure of below 10^{-10} mbar, the usually do not undergo any collisions during this time. As indicated in Figure 1, however, we have the option to introduce a collision gas, for example HCl, into the ultra high vacuum region at any desired, well-controlled and stable pressure, typically around 4.0×10^{-8} mbar; this then yields about five collisions with the stored clusters per second.

Blackbody-radiation-induced fragmentation of cluster ions: In the absence of collisions, the dominant interaction of the clusters with their environment is an absorption of black-body infrared radiation from the apparatus walls, as was clearly demonstrated by numerous studies in several laboratories.[6] Since the clusters are not stable at room temperature, as their temperature rises, they have to cool themselves by evaporating one water molecule at a time. The rate of the solvent "evaporation" is roughly proportional to n, the number of ligands.[6c,f] This proportionality can easily be understood: In essence each time before the cluster can evaporate a water ligand, it must absorb an energy amount approximately equivalent to its sublimation enthalpy. Since the water ligands are the absorbing "chromophores", the rates of energy absorption by the clusters, and thus also the rates of their fragmentation, must be roughly proportional to their number, n. Details like local deviations of the ligand binding energy from the sublimation enthalpy are then reflected in the deviations from the overall linear dependence. This millisecond timescale fragmentation process on the one hand limits the size of clusters which can be conveniently studied, but on the other hand allows a gentle removal of the ligand molecules one by one. The ionic "droplets" solvated on a nanometer scale are, thus, a very useful medium, in which one can explore a wide range of aqueous reactions, and investigate conveniently the effects of the loss of the stabilizing solvent upon the cluster chemistry and properties.

Redox reactions in aqueous clusters: While "simple" systems like protonated water clusters $H(H_2O)_n{}^+$ respond to radiative heating exclusively by evaporative cooling, hydrated metal ions in oxidation state (I) can also undergo redox reactions, in which the metal is oxidized to a more stable oxidation number, and hydrogen is reduced and lost from the cluster. These intracluster reactions and the loss of hydrogen are easily identified by the characteristic mass change they induce, and the high-resolution mass measurement by the FT-ICR technique allows for the unambigous identification of the products.

As an example we can mention recent studies by several groups of hydrated M^+ ions of main-group elements such as Mg,[7] Ca,[8] or Al.[3] Even though these metals usually do not occur in their compounds as monovalent, the hydrated cation clusters are easily produced by using the laser vaporization source. Their stability, however, is a sensitive function of the size of the solvation shell. The $Mg(H_2O)_n{}^+$ ions are observed for $n \leq 5$ and for $n \geq 17$, but in the intermediate range, only clusters containing hydroxide of divalent magnesium, $Mg^{II}OH(H_2O)_n{}^+$ are detected. Our FT-ICR studies[7d,e] have revealed that a large trapped $Mg(H_2O)_n{}^+$ cluster loses water ligands until the $n \approx 17-20$ limit is reached. In this region a competing process appears, in which the magnesium(I) ions are oxidized to Mg^{II} and water ligands are reduced, yielding an $MgOH^+$ hydroxide core ion and an atomic hydrogen atom [Eq. (1)]:

$$Mg^I(H_2O)_n{}^+ + h\nu \rightarrow Mg^{II}OH(H_2O)_{n-2}{}^+ + H_2O + H \qquad 17 \leq n \leq 20 \qquad (1)$$

Very similar behavior is also observed in the case of aluminum, with again very large and very small clusters seeming stable. An oxidation of Al^I to Al^{III} is observed in the intermediate range, with the development, in this case, of molecular hydrogen (H_2).[3] Recent calculations[9] indicate that the oxidation of Al^I to Al^{III} takes place upon solvation of the singly-charged ion in a sufficiently large cluster, and a hydride–hydroxide intermediate is formed presumably on a sub-millisecond timescale [Eq. (2)]:

$$Al^I(H_2O)_{n+m}{}^+ \rightarrow HAl^{III}OH_{n-1}{}^+ + m\,H_2O \qquad m \approx 5,\ n \geq 10 \qquad (2)$$

The presence of the aluminum hydride–hydroxide species seems to be a necessary condition for the formation of molecular hydrogen. The calculations[9] confirm our early suggestion that hydrogen formation proceeds through a combination of O–H insertion and proton transfer.[3a] In a second redox reaction, the hydride recombines with a proton, forming molecular hydrogen and an additional hydroxide ligand. The hydride is oxidized, and the proton is reduced, both to elementary hydrogen [Eq. (3)]:

$$HAl^{III}OH(H_2O)^+_{n-1} + h\nu \rightarrow Al^{III}(OH)_2(H_2O)^+_{n-k-2} + k\,H_2O + H_2 \qquad k=2,3,\ 11 \leq n \leq 24 \tag{3}$$

Figure 2 summarizes the processes observed so far with hydrated metal ions upon radiative heating: the cluster may decay by the loss of a single water molecule, or undergo intracluster redox reactions to adopt a more stable oxidation state of the metal.

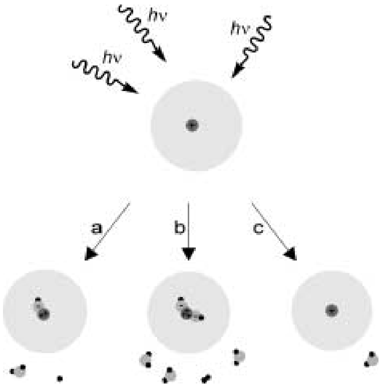

Figure 2. Possible reaction pathways of hydrated metal(I) cations in a collision-free environment. Ambient black-body radiation from the apparatus walls heats the nanodroplet, which gradually obtains the internal energy for overcoming reaction barriers to: a) Oxidation of M^I to M^{II} and reduction of water leading to elimination of atomic hydrogen. b) Oxidation of M^I to M^{III} and reduction of two water molecules leading to elimination of molecular hydrogen, proceeding presumably via a hydrated $HM^{III}OH^+$ intermediate. c) Evaporation of water without redox reaction.

Formation of hydrated transition-metal cations: In view of the ability of the FT-ICR cluster source to produce hydrated M^+ ions, even for elements that usually do not occur in their compounds as monovalent, it appeared of interest to extend the study to transition metals in order to explore their aqueous chemistry in the oxidation state (I). The experiments have indeed demonstrated, that with the exception of titanium, for most of the transition metals we studied such $M(H_2O)_n{}^+$ clusters could be prepared, stored, and they could survive for an appreciable length of time trapped in the ICR trap. The laser vaporization source produced readily hydrated V^+, Cr^+, Mn^+, Fe^+, Co^+, Ni^+, and Cu^+, solvated with typically up to about 50 water ligands.[4, 5] Interestingly, however, the rich redox chemistry, which might perhaps be expected based on the observations with main group elements like Mg^+ or Al^+ was not detected. The hydrated cations in the unusual oxidation state (I) could be prepared remarkably free from oxides or hydroxides, and with the exception of vanadium discussed in the next section, they appeared to be stable with respect to intracluster oxidation over the entire range of n values studied, showing no inclination towards reacting with water to form hydroxides and eliminate hydrogen. Since we are limited to mass spectrometric detection, a hydride–hydroxide formation similar to the reaction in Equation (2) is in principle possible.

Clearly, based on the above discussion, these ions, which are unknown in bulk solutions, must owe their stability, at least on the timescale of the ICR experiment of up to 100 s, to the fact that neither of the reactions that apparently lead to their destruction in bulk solutions can occur readily in finite clusters. The disproportionation can evidently not take place, since invariably only a single metal ion is present, and, similarly, in the relatively small clusters there are no other ions like H^+ or OH^- that might catalyze or accelerate the oxidation of the metal. Starting with a distribution of large clusters, the only process which was observed, with the exception of the vanadium experiments, was a cluster fragmentation.

The absence of any intracluster reaction is perhaps most surprising in the case of Mn^+ and Fe^+, whose ground states have the same valence electron configuration as Mg^+, with a single 4s electron. In the case of the Mn and Fe ions it is, however, conceivable, that the solvation affects the stability of the metal orbitals and induces promotion of the 4s electron into the 3d level. In fact, this has been proposed for Fe^+ based on several experimental and theoretical results.[10]

Intracluster redox reactions of $V(H_2O)_n{}^+$ and their size dependence: Among the first row $M(H_2O)_n{}^+$ clusters studied, vanadium was the only one to exhibit the redox reactions that one might expect for a transition metal. The titanium ion is, on the other hand, apparently so reactive that only the hydroxide species ($Ti(OH)_2(H_2O)_n{}^+$) are observed. The monovalent cations of vanadium in bulk solutions are only known when stabilized by organic ligands. For instance, $V(bipy)_3{}^+$, as well as the octahedral hexahydrate ions $V(H_2O)_6{}^{2+}$ and $V(H_2O)_6{}^{3+}$ are all well characterized.[1] On the other hand, the monovalent $V(H_2O)_n{}^+$ ions could readily be prepared in the gas phase, but the investigation of size-selected clusters revealed that, in addition to pure fragmentation and depending on the cluster size, also oxidation to both V^{II} and V^{III} is possible [Eqs. (4)–(6)]:[4]

$$V(H_2O)_n{}^+ + h\nu \rightarrow V^I(H_2O)_n{}^+ + H_2O \qquad 4 \leq n \tag{4}$$

$$\rightarrow V^{II}(OH)(H_2O)_{n-1-k}{}^+ + k\,H_2O + H \qquad 9 \leq n \leq 12,\ k=0,1 \tag{5}$$

$$\rightarrow V^{III}(OH)_2(H_2O)_{n-2-k}{}^+ + k\,H_2O + H_2 \qquad 9 \leq n \leq 23,\ n \neq 15,\ k=2,3 \tag{6}$$

Once formed, $V^{II}OH(H_2O)_n{}^+$ species do not further react to $V^{III}(OH)_2{}^+(H_2O)_m$, that is, a consecutive elimination of two hydrogen atoms is not observed. Similar to the aluminum case, a hydride–hydroxide intermediate $HV^{III}OH(H_2O)_{n-1}{}^+$ is possibly involved in the formation of molecular hydrogen. Atomic hydrogen, on the other hand, is probably not eliminated from these intermediates, as this would require reduction of the metal and oxidation of the hydride ion. Since the formation of atomic and molecular hydrogen compete, the situation is considerably more complicated than with aluminum.

Figure 3 displays graphically the rate constants of the three competing processes. Although formation of molecular hydrogen is the most exothermic process, as revealed clearly by

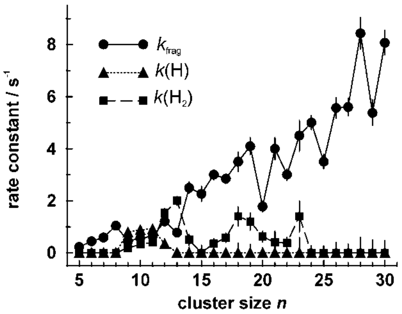

Figure 3. First-order rate constants of the black body radiation induced unimolecular reactions of size-selected $V(H_2O)_n^+$, $n = 5-30$. Very small hydrated vanadium ions $V(H_2O)_n^+$, $n = 5-8$, and very large clusters, $n = 24-30$, only fragment by losing water molecules. Small clusters, $n = 9-11$, preferentially decay by forming atomic hydrogen, but also water evaporation or formation of molecular hydrogen is possible. For $n = 12$ and $n = 13$, formation of molecular hydrogen is the most efficient reaction channel. For $n = 12$ formation of atomic hydrogen is observed to a small extent. Clusters of size $14 \leq n \leq 23$ preferentially fragment, but also formation of molecular hydrogen is observed. Reproduced from ref. [4] by permission of the PCCP Owner Societies.

the concomitant evaporation of up to three water molecules, it is usually not the dominant one. On the contrary, even in the narrow range of cluster sizes in which it occurs at all, the only quite weakly exothermic, or possibly even slightly endothermic oxidation to V^{II} with the formation of an atomic hydrogen, is by far the prevailing reaction.

The number of water molecules that are evaporated serves as a rough calorimeter providing information about the overall exothermicity of the process, while the branching ratios provide insights into the activation energies and entropic contributions. Formation of the thermochemically unfavorable hydrogen atom is apparently aided by both a facile mechanism and a low activation energy, while the much more exothermic pathway, formation of molecular hydrogen, appears to be kinetically hindered by a complex mechanism and a high barrier. Elimination of a water molecule presumably represents the simplest reaction pathway, but at the same time confronts the highest activation energy.

In contrast with the main group elements, which undergo one specific redox reaction to adopt their preferred oxidation state, vanadium as a transition metal can react to yield two different oxidation states by eliminating either H or H_2 from the hydrated metal cluster. These relatively small systems are ideal models for computational simulations of the redox chemistry of transition metals, and will thus surely aid a molecular understanding of one of the most basic processes in electrochemistry.

Dissolving Reactants in a Nanodroplet

The range of reactions that can be studied in such ionic "nanodroplets" is greatly extended by the possibility to "dissolve" in them suitable gaseous reactants.[2a,b,e, 11] Our previous experiments have shown, that when gas-phase species like HCl are introduced into the ICR instrument vacuum, typically at pressures corresponding to a few collisions per second, these can easily be exchanged for the water ligands.[11a,b] Interestingly, however, even though HCl dissolves exothermically in bulk water, one finds that regardless of whether M^+ is a metal ion, for example, Na^+, or a proton, H^+, the hydrogen halides are taken up by the $M(H_2O)_n^+$ clusters only if n is at least about eleven. Smaller clusters with $n \leq 11$ do not react at all, since a sufficient amount of solvent needs to be present to allow an ionic dissolution and dissociation of the hydrogen halide.

Conversely, upon fragmentation and evaporation of larger clusters in which one or more hydrogen halide molecules have already been dissolved, when this $n \leq 11$ limit is reached, the H^+ and Cl^- ions can no longer be stabilized and they recombine. As depicted in Figure 4a, the resulting covalent HCl molecule, which can form only one donor hydrogen bond, in contrast to the stronger bound water ligands, evaporates from the cluster. Again a pure hydrated cluster ion is eventually left behind.

Precipitation of insoluble salts in nanodroplets: A qualitatively different behavior is observed, when, instead of H^+ or Na^+, the central ion is Ag^+.[11b] In this case, the HCl is efficiently taken up by the cluster for $n \geq 5$, which is surely not sufficient to ionically dissolve HCl and at the same time stabilize Ag^+. Also when larger $Ag(HCl)(H_2O)_n^+$ clusters are allowed to fragment, HCl is lost only after the number of water ligands is reduced to about $n = 4$. A clear difference between the compounds involved lies in their solubilities. While HCl as well as alkali halides are highly soluble in water, AgCl or AgBr are among the most insoluble compounds. Upon introducing HCl into a cluster that contains an Ag^+ ion, a process analogous to precipitation from bulk solutions apparently takes place, and a discrete AgCl molecule with a strong covalent character forms, as indicated in Figure 4b. The silver-containing clusters are therefore more accurately formulated as $H^+(H_2O)_n(AgCl)$. The evaporation of HCl from clusters that contain both H^+ and AgCl is of interest, when upon their fragmentation the number of ligands is reduced to about $n = 4$. In the gas phase much more energy (1312 kJ mol^{-1}) is required to ionize a hydrogen atom, compared with the ionization energy of Ag (736 kJ mol^{-1}). In an aqueous solution the situation is completely reversed due to the enormous solvation energy of H^+. As the water ligands are lost, however, the stabilization energy of the proton gradually decreases. Somewhere around $n = 4$ the incompletely solvated H^+ withdraws sufficient electron density from the AgCl molecule to destabilize the considerably covalent Ag–Cl bond. Upon further solvent loss the bond breaks, leaving behind a hydrated Ag^+ ion, with the newly formed HCl molecule evaporating from the cluster.

Acid–base catalysis in water clusters: The ionic nanodroplets are also an interesting medium for demonstrating the catalytic effect of introducing additional ions into solutions by dissolving HCl in them, and investigating their effect upon the course of intracluster reactions. As an example, one can again consider the above-discussed $M(H_2O)_n^+$ clusters containing magnesium or aluminum ions. Regardless of the cluster size, almost immediately upon "dissolving" the hydrogen halide,

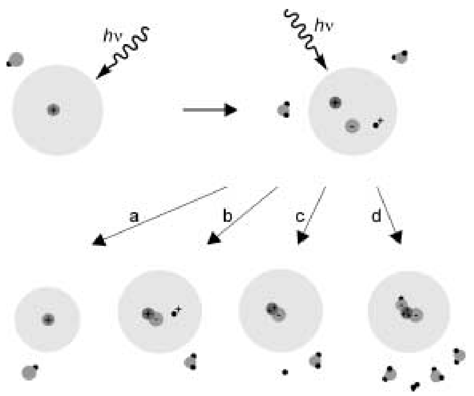

Figure 4. Possible reaction pathways of hydrated metal(I) cations with HCl. In a reactive collision with HCl, the molecule is ionically dissolved in the cluster, and typically two water molecules are released due to the reaction enthalpy. a) If no precipitation or redox reaction takes place, three individual ions need to be solvated by water. Solvation breaks down at fairly large sizes of the cluster, and a molecule of HCl is released. b) No redox reaction takes place when a single molecule of M^ICl precipitates in the strongly acidic water cluster with $pH \leq 0$. Water molecules are gradually lost until the cluster becomes very small. c) The metal ion is oxidized to M^{II}, thereby reducing the proton to atomic hydrogen, which is eliminated together with typically two water molecules. d) If the preferred oxidation state of the metal is (III), the proton and a hydrogen atom in a water molecule are both reduced, releasing molecular hydrogen and typically three water molecules from the cluster. This reaction can involve a hydrated $HM^{III}OH^+$ intermediate, which may form before dissolution of HCl in the cluster.

atomic hydrogen is eliminated from $Mg(H_2O)_n^+$,[7e] and molecular hydrogen from $Al(H_2O)_n^+$.[3b] In clusters containing dissolved acid, the upper limit for the hydrogen elimination observed in the "pure" hydrated clusters disappears, and the metal oxidation becomes mass spectrometrically observable even for n values well beyond this limit. Oxidation of the aluminum probably takes place even before dissolution of the HCl by formation of an $HAl^{III}OH^+$ intermediate.[9] As suggested previously based on the experimental observations,[3b] the H_2 elimination upon introduction of the acid is the result of a reaction of the hydride with the proton. The redox reactions [Eqs. (7) and (8)] are depicted in Figure 4c and d:

$$Mg^I(H_2O)_n^+ + HCl \rightarrow Mg^{II}Cl(H_2O)_{n-k}^+ + k\,H_2O + H \qquad k \approx 2 \tag{7}$$

$$HAl^{III}OH(H_2O)_n^+ + HCl \rightarrow Al^{III}(OH)Cl(H_2O)_{n-k}^+ + k\,H_2O + H_2 \qquad k \approx 3-4 \tag{8}$$

Transition metal(I) chlorides: Based on this experience with the main-group elements, one might have expected that introducing an acid species like HCl, which dissolves with ionization, into the clusters containing transition-metal monocations will again induce and accelerate their oxidation. Experimentally one finds, however, that while the dissolution of the acid again proceeds efficiently with the reaction enthalpy heating the cluster, no evidence for oxidation of the transition metals is observed.[5] Typically, two or three water molecules evaporate when the hydrogen halide is dissolved, but with the exception of V^+, no redox chemistry takes place, and neither hydrogen atoms nor H_2 molecules are released from the cluster.[5] Since the hydrides would presumably react with the proton to form molecular hydrogen, the absence of H_2 elimination upon dissolution of HCl is also evidence that no $HM^{III}OH(H_2O)_{n-1}^+$ hydride–hydroxide species are present for M = Cr, Mn, Fe, Co, Ni, and Cu.

A clue for interpreting this result is again provided, when one examines the subsequent black-body or collision-induced fragmentation of the resulting $M^+(H_2O)_n(HCl)$ clusters. One observes that unlike the clusters that contain H^+ or Na^+ central ions, but similar to those containing Ag^+, the last HCl molecule is not lost near $n = 11$, but depending on the specific metal, only around $n = 3-7$, as listed in Table 1. A most reasonable interpretation of this behavior is, similar to AgCl, that in the case of the monovalent transition-metal ions of Cr^I, Mn^I, Fe^I, Co^I, Ni^I and Cu^I, highly insoluble monochlorides are formed. As soon as the hydrogen halide is introduced into the cluster, a single molecule of the respective metal chloride "precipitates" in the droplet. The monocations do not reduce water, most probably because the rate of the chloride formation is much faster than that of the redox reaction.

Table 1. Precipitate, number of water molecules n_{min} when last HCl or HBr is eliminated, ionization potential (IP) of the metal or hydrogen, and, if known, the solubility product in bulk solution. Reproduced with permission from ref. [5], © American Chemical Society.

Precipitate	n_{min}	IP [eV]	Solubility product
CrCl	4	6.77	
MnCl	≤3	7.43	
FeCl	3	7.90	
CoCl	6	7.88	
NiCl	7	7.63	
CuCl	5	7.73	1.7×10^{-7}
NaCl	12	5.14	3.7×10^{1}
AgCl	4	7.58	1.8×10^{-10}
AgBr	3	7.58	5.4×10^{-13}
HCl	11	13.60	

After intake of the hydrogen halide, the clusters are therefore again more appropriately formulated as $H^+(H_2O)_n(M^ICl)$, with the charge formally residing on the solvated proton. Like in the case of hydrated Ag^I, as the fragmentation proceeds the solvated proton is more and more destabilized, and at a certain critical cluster size becomes acidic enough to abstract the chloride ion from the discrete M^ICl molecule. Speaking in terms of solution chemistry: with a decreasing number of water molecules, the cluster becomes more and more acidic. Analogous to bulk solution, in which solubility increases with decreasing pH, the metal-chloride single-molecule precipitate becomes soluble at a certain critical pH value, and the reforming HCl can evaporate from the cluster. It is illustrative to keep in mind that pH = 0 amounts to one proton per 55 water molecules in solution.

Outlook

Previous work has shown that chemistry as known from bulk aqueous solutions proceeds on the single-ion level in small water clusters. With the most recent results on hydrated transition-metal ions, we do the next step to investigate aqueous chemistry of species that are unstable in bulk solution. The perhaps surprising conclusion from this study is that aqueous M^I of first-row transition metals are far less readily oxidized than expected. To explore their redox chemistry further, experiments with more strongly oxidizing agents, such as HNO_3, SO_2, SO_3, or O_3 would be interesting. Changes of the electronic state of the metal with cluster size and mass spectrometrically invisible redox reactions have to be probed by optical spectroscopy. The influence of relativistic effects can be studied with third-row transition metal ions. Using nonaqueous nanosolutions, that is, putting the transition metal ion into clusters of DMSO or benzene, offers the key to a completely new branch of organometallic chemistry. In each case, the clusters serve as nanoreactors; this allows for the stabilization of a variety of elusive species and investigation of their chemistry in the solution environment. While the gas-phase cluster chemistry may not immediately lead to new products, it has the potential to reveal large new areas of fundamental transition metal chemistry.

Acknowledgement

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