Single-Molecule Precipitation of Transition Metal(I) Chlorides in Water Clusters

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Aqueous chemistry of uncomplexed transition metals in oxidation state +I is virtually unknown, since the singly charged metal ions are unstable in bulk aqueous media.[1] Their instability is in part due to the much higher hydration energy of the M^{2+} ions, which for instance in copper is known to lead to a rapid disproportionation $2Cu^I \leftrightarrow Cu^{II} + Cu(s)$.[1] In some cases the +I state can be stabilized by complexation, and in fact the Cu^{II}/Cu^I couple is believed to be important in a number of electron-transfer processes in enzymes and proteins.[2] We demonstrate, however, that clusters with typically 20–50 water molecules containing the uncomplexed, singly charged metal ion can be stabilized for at least several seconds in ultrahigh vacuum, and their chemistry in collisions with single reactant molecules can be investigated.

We have previously established that reactions in such clusters proceed comparably to those in bulk aqueous solutions,[3–5] and macroscopic concepts such as pH[5] or solubility[4] can be transferred to the single-ion level. Precipitation reactions serve as the first application of water clusters in the study of aqueous transition metal(I) chemistry.

Hydrated metal cations of the type $M(H_2O)_n^+$, $n \leq 50$, are generated by laser vaporization of the metal followed by a supersonic expansion of the hot plasma in a helium/water mixture.[6] The species produced are trapped in ultrahigh vacuum in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer, where their temperature is controlled by competition between evaporative cooling and heating by blackbody radiation[7–11] and collisions. Neutral reactants are introduced into the ICR cell at pressures corresponding to about five collisions between the ionic cluster and the neutral gas molecule per second.

Figure 1 illustrates how the reaction of hydrated ions with HCl proceeds over a time span of typically 50 s. The HCl molecules collide with the ionic clusters, and about 10% of the collisions are reactive, with the hydrochloric acid being taken up and ionically dissolved in the cluster.[4,12] The enthalpy of this reaction is released and heats the cluster, which in turn leads to evaporative cooling by loss of two to three water molecules. Depending on the number of available water ligands, additional HCl molecules may be absorbed into the water cluster. Conversely, as the solvent molecules are continuously removed from the clusters due to collisional and radiative heating, ultimately the ionic solution becomes destabilized, and an HCl molecule may evaporate from the cluster.

Once the HCl molecule is dissolved in the water cluster, solution-phase chemical reactions can take place. For instance, the proton may oxidize the metal ion, with (a) atomic or (b) molecular hydrogen being released, as we previously observed for hydrated Mg^+ or Al^+ ions,[13,14] respectively. An alternative possibility is the precipitation of a single molecule of the metal chloride in the solution (c), which does not leave an immediate signature in the
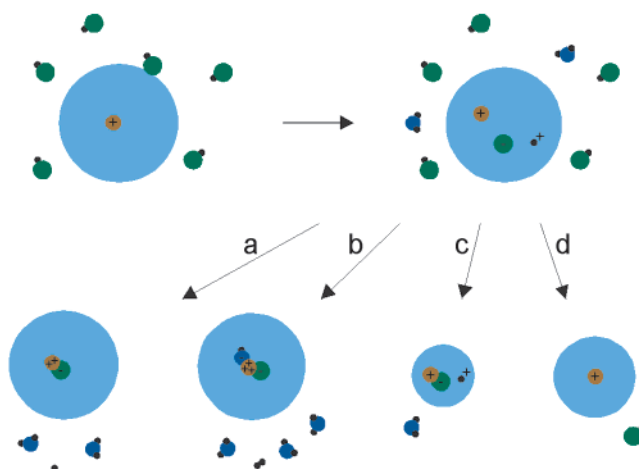

Figure 1. Possible reaction pathways of hydrated metal(I) cations with HCl. In a reactive collision with HCl, the molecule is ionically dissolved in the cluster, and typically two water molecules are released due to the reaction enthalpy. (a) The metal ion is oxidized to +II, thereby reducing the proton to atomic hydrogen, which is eliminated together with typically two water molecules. (b) 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. (c) No redox reaction takes place when a single molecule of M(I)-Cl precipitates in the strongly acidic water cluster with pH $\leq$ 0. Water molecules are gradually lost until the cluster becomes very small. (d) 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.

mass spectrum. By monitoring the subsequent reactions and the ligand evaporation as a function of time, however, one can unmistakably diagnose if the salt remains ionized, or forms a single molecule "precipitate".[4]

In a cluster containing a metal cation, which forms a highly soluble chloride such as sodium, three ions, that is, Na^+, H^+, and Cl^-, have to be individually solvated. Similarly, in a protonated water cluster containing dissolved HCl, three ions, $2H^+$ and Cl^-, are present. As the cluster is gradually heated and desolvated, eventually the H^+ and Cl^- recombine to form HCl, and the covalent hydrogen chloride evaporates from the $M(HCl)(H_2O)_n^+$ cluster (d). This occurs around $n = 12$.[4] A quite different situation was found for Ag^+, which forms an insoluble chloride. In this case the last HCl is lost when only four molecules of water are left, $n = 4$, surely too little solvent to hydrate the three separate ions.[4] One can conclude from this observation that only a single H^+ ion is present and that the covalent AgCl molecule formed as a precipitate in the solution. Thus, the number of water molecules n at which HCl is eliminated from the $M(HCl)(H_2O)_n^+$ cluster in the desolvation process can be viewed as a measure of solubility of the

Table 1. Precipitate, Number of Water Molecules n_{min} When Last HCl Is Eliminated, Ionization Potential of the Metal, and, If Known, the Solubility Product in Bulk Solution

precipitate	n_{min}	I. P. [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} [c]
NaCl	12[a]	5.14	$\sim 3.7 \times 10^{1}$ [d]
AgCl	4[a]	7.58	1.8×10^{-10} [c]
AgBr	3[b]	7.58	5.4×10^{-13} [c]
HCl	11	13.60	

[a] Reference 4. [b] Reference 18. [c] Reference 15. [d] Reference 17.

corresponding chloride. The observations correlate nicely with solubility products known from bulk solutions, with sodium chloride being highly soluble, while silver chloride is the least soluble metal-(I) chloride in the literature.[15] Similar minimum size values for HCl uptake by water clusters containing H^+ and Na^+ have recently been observed in flow reactor studies,[16] which indicates that the minimum size of the cluster is an intrinsic property of the reaction system.

The first row transition metals V−Cu are known to occur in a variety of oxidation states, but with the possible exception of Cu, they do not form stable uncomplexed metal(I) ions in aqueous solutions. Despite that, however, we find that from the metals studied here, only V^+ ions are readily oxidized upon reaction with HCl with evolution of hydrogen. If one considers the standard electrochemical series, and the potentials needed to oxidize the metals, one finds the order Mg < Al < V < Mn < Cr < Fe < Co < Ni < Cu < Ag. It therefore seems reasonable that the first three of these elements exhibit a redox chemistry in clusters, while the others do not, although the difference between the V and Mn oxidation potentials is quite small.

Unlike Mg^+, Al^+, and V^+, which are, upon reaction with HCl, readily oxidized with the evolution of atomic or molecular hydrogen, the ions of Cr, Mn, Fe, Co, Ni, and Cu do not change their oxidation state even in the presence of the strongly corrosive hydrochloric acid; instead they react, similar to silver monochloride, without changing their oxidation state. The resulting cluster containing the chloride "precipitate" and a proton then gradually loses water ligands. When some specific number of water ligands n, which is characteristic of the particular metal, is reached, an HCl molecule is lost, and a hydrated monovalent metal cation $M^+(H_2O)_n$ remains. It is interesting to consider the charge transfer between H^+ and a metal chloride occurring in the cluster:

$$H^+(H_2O)_n(MCl) \rightarrow H.MCl^+(H_2O)_n \rightarrow M^+(H_2O)_n + HCl$$
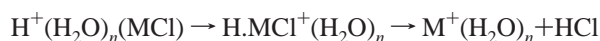
This reaction is strongly exothermic in the gas phase ($n = 0$), but in view of the enormous lowering of the H atom ionization potential due to solvation, endothermic in bulk solution ($n = \infty$). Clearly, the thermochemistry of this reaction depends on the available solvent and has to reverse sign as n is reduced and solvent is lost. To predict the exact value of n where this will occur for a specific metal is difficult, since it will depend not only on its ionization potential, but also on the strength of the MCl bond, the preferred coordination of the metal cation, and on its hydration enthalpy.

Table 1 gives the number n_{min} of solvent molecules remaining when the last HCl is eliminated for the precipitation reactions investigated in the present work and compares it with cations studied previously. The table also gives the ionization potentials of the metals, and where available, the solubility constant of the salt in water. It is interesting to note that the solubilities correlate qualitatively with the values of n_{min}. If this correlation has some broader validity, one could predict an extremely low solubility for MnCl which does not eliminate HCl even when $n = 3$ is reached, followed by FeCl, where the HCl loss at $n = 3$ is only observable after $t \approx 0.50$ s. Conversely, it would suggest for NiCl and CoCl solubilities higher than that of CuCl.

The low solubility of AgCl is usually explained by the strongly covalent character of the silver−chlorine interaction, and it is therefore perhaps quite reasonable that also other transition metals, with their partly filled d-shell should form relatively insoluble metal(I) chlorides. More surprising may appear our observation, that with the exception of vanadium, the singly ionized cations of the first-row transition metals are not readily oxidized into their more favored oxidation states, even in the presence of hydrochloric acid. Perhaps the rapid formation of a single-molecule chloride "precipitate" hinders the oxidation reaction kinetically, so that although thermodynamically favored, it does not occur on the ≈ 100 s time scale of our experiment.

Our study shows that one can generate transition metal(I) cations in water clusters and investigate their precipitation or other reactions on the single-ion level. This opens up the new experimental field of aqueous transition metal(I) chemistry and provides the key to a previously inaccessible realm of redox reactions and electrochemistry.

Supporting Information Available: Mass spectra of the reaction products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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