Generation of hydrated iodide clusters I − (H 2O) n by laser vaporization, their fragmentation and reactions with HCl

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Generation of hydrated iodide clusters $I^-(H_2O)_n$ by laser vaporization, their fragmentation and reactions with HCl

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Abstract

Hydrated halide anions $I^-(H_2O)_n$, $n = 0–25$, were generated in a laser vaporization source by laser vaporization of solid CsI and water expansion. An investigation of the black-body radiation-induced fragmentation of size-selected clusters ($n = 1–12$) under collision-free conditions in a Fourier-transform–ion cyclotron resonance mass spectrometer revealed an overall $k \sim n$ unimolecular rate constant dependence as has been observed before with other hydrated ions. Adding HCl as reaction gas into the cell region, a series of subsequent ligand exchange and fragmentation reactions result in terminal anions of the type $I^-(HCl)_n$. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The understanding of solvation phenomena is of considerable importance for understanding the basic properties of both bulk solutions and finite cluster systems. Experimental [1–3] and theoretical [4–9] work, performed to study the solvation of charged solute embedded in water clusters, demonstrates a rich dynamical and structural behavior.

Dunbar et al. [10] measured the fragmentation kinetics of the gas-phase cluster ions $Cl^-(H_2O)_2$ and $Cl^-(H_2O)_3$ in the zero-pressure limit. They used thermal black-body radiation, which induces fragmentation by absorbing photons from the walls of the apparatus to obtain the dissociation rate constants. The experimental results were compared with theoretical predictions and kinetic modeling. The group of Okumura used infrared-induced vibrational

predissociation to obtain infrared spectra of cluster ions. They recorded the spectrum of $I^-(H_2O)$ and observed a hydrogen-bonded OH stretch and a free OH stretch, indicating that H_2O forms a single hydrogen bond with the iodide anion [11]. Markovitch and coworkers [12,13] used photoelectron spectroscopy to obtain spectra of I^- solvated with up to 15 water molecules. They found an abrupt decrease in the electrostatic stabilization energy after $n = 6$ and assumed therefore a central position of the iodine anion, with the closure of the first solvation shell at $n = 6$. Jortner and coworkers [14–16] presented ab initio molecular orbital calculations of the vertical ionization potentials of surface- and interior-hydrated anion structures. The comparison of the experimental results [12,13] and the calculated differential ionization potential shifts are in agreement with the assumed internal solvation and shell closure at $n = 6$. Perera and Berkowitz [17] performed molecular dynamics computer simulations on

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$Cl^-(H_2O)_n$ clusters, $n = 2$–15. From their calculations they derive the stabilization energies of the anion in the cluster and compare these with the corresponding values obtained from photodetachment spectra of $X^-(H_2O)_n$ clusters (X = Cl, Br or I). The comparison suggests that halide anions are not solvated in small water clusters, but are attached to the water cluster instead. Coe [18,19] used a new least-squares method, based on cluster ion data and well-known bulk constraints, to determine the single ion bulk solvation enthalpies and presented a simple model for estimating the solvation enthalpy of any size cluster ion. This model supports the view that the large halide ions are not solvated internally by small water clusters. The approach predicts that about 46 water molecules are required to internalize I^-.

We recently succeeded in producing a water solvated halide with our laser vaporization source. The study of black-body radiation induced fragmentation of $I^-(H_2O)_n$, $n = 0$–25 and their reactivity with hydrogen chloride can provide new insights into the question of halide ion solvation.

2. Experimental

The modified Fourier transform–ion cyclotron resonance (FT–ICR) mass spectrometer CMS47X on which the experiments were performed was described in detail before [20,21], so that only the features which are pertinent to the present experiments need to be discussed here.

The iodine anions were generated by vaporizing discs of compressed granular caesium iodide (Merck, 99.5% +) with the focussed 532 nm radiation of a Continuum Surelite II Nd:YAG laser (spot size on target ≈ 500 μm). The laser was operated at 10 Hz with 10–20 mJ in 5 ns pulses producing the initial plasma. The laser vaporization was synchronized with pulses of helium carrier gas supplied by a home-built piezoelectric valve with an opening time of about 50 μs. The helium was seeded with water vapour in a home-built zeolith-trap. Typical pressures of water and helium were 35 mbar (vapor pressure of water at 27°C) and 10 bar, respectively. The initially hot salt plasma entrained in the helium–water pulse was cooled by flowing through a confining channel (40 mm, 2 mm ID) and subse-

quent supersonic expansion into high vacuum, typically 10^{-6} mbar, resulted in cluster formation.

The advantage of vaporizing a solid target is that the carrier gas inlet system is not contaminated or attacked by toxical or corrosive substances. In addition, a change from one salt target to another is possible within a short period of time.

The cluster ions, produced without postionization, were accelerated downstream, skimmed with a 100 μm skimmer, transferred into the high-field region of the superconducting magnet, decelerated, and stored inside the ICR 'infinity-cell' [22] at a pressure of about 6×10^{-10} mbar. The low pressure used in the present study corresponds to one collision of a cluster ion with a residual gas molecule about every 100 s. To improve the cluster ion signals, up to 20 injection cycles were accumulated at the 10 Hz repetition rate of the Nd:YAG laser, prior to the reaction delay and detection. The vacuum chamber enclosing the ICR cell was cooled by a flow of water through the cooling jacket, resulting in a constant temperature of the apparatus walls of $T = 291 \pm 5$ K. The hydrochloric acid reactant gas, HCl (Aldrich, 99% +), was used without further purification and introduced into the ultra-high vacuum region via a needle valve, while maintaining a constant pressure of about 10^{-8} mbar.

3. Results and discussion

3.1. Fragmentation

The black-body radiation offers a useful universal tool for gently removing the solvent molecules, one after the other, from the hydrated ionic system [23–27]. A typical initial cluster distribution produced by the laser vaporization source is shown in Fig. 1. Essentially it consists of $I^-(H_2O)_n$ clusters, $n = 0$–25, with minor contributions of other solvated $X^-(H_2O)_n$ species, X = I_2, CsI, CsI_2 with up to $n = 3$. These impurities are denoted in Fig. 1 by filled circles. The cluster size distribution and the amount of the impurities are easily shifted over a broad range by varying the source conditions. Depending on the parameters, either larger unsolvated hetero-cluster sizes, or much wider distributions of the hydrated impurity species were obtained. What
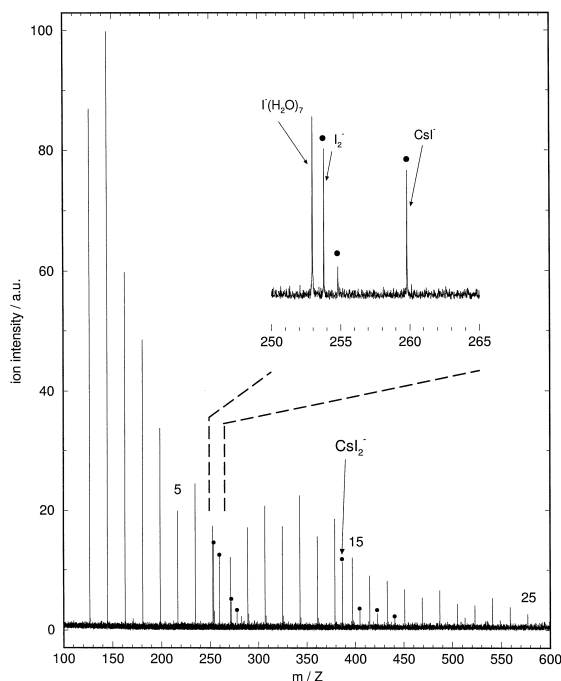
Fig. 1. Initial cluster distribution of $I^-(H_2O)_n$, $n = 0-25$, produced by the laser vaporization source. I_2^-, CsI^- and CsI_2^- impurities are denoted by filled circles. Pressure in the ICR cell $\sim 6 \times 10^{-10}$ mbar.

proved to be the most critical parameter was the delay between the trigger of the piezo-valve and the Q-switch of the Nd:YAG laser.

To study the stability of $I^-(H_2O)_n$, the clusters were stored in the ICR cell and exposed to the black-body infrared radiation at variable reaction delays. The observed fragmentation in the essentially collision-free environment of about 6×10^{-10} mbar can be followed in Fig. 2, showing the changes in the cluster distribution after 0.5, 8 and 120 s. The most apparent effect is the shift of the whole distribution to smaller cluster sizes. After a reaction time of 120 s in Fig. 2c, the more or less 'final' distribution consisting of I^-, $I^-(H_2O)$, $I^-(H_2O)_2$ and small amounts of the I_2^- and CsI^- impurities can be seen. On the timescale of our experiments only minor changes in the distribution of the products can be observed with further increasing the reaction delay.

To examine this cluster fragmentation and its dependence upon the cluster size in more detail, one can take advantage of the ability of the FT–ICR technique to mass select a cluster of a particular size,

and record educt fragment intensities as a function of time. The observed decays of such size-selected clusters were then fitted by first-order reaction kinetics. The fragmentation rates of the $n = 1-12$ $I^-(H_2O)_n$ clusters obtained by this procedure are shown as open circles in Fig. 3. As shown by the solid line, representing a linear regression with the equation: $k = 0.17(n - 1.53)$ s^{-1}, they exhibit clearly the overall linear n-dependence reported before for other hydrated ions [27,28]. The unimolecular rate constants again increase linearly with the number of infrared absorbers. The smallest cluster $I^-(H_2O)$ which nearly do not fragment, eventually reach equilibrium with the temperature of the apparatus walls. The temperature of the larger clusters is determined by the competition between radiative heating and evaporative cooling [27].

Cheshnovsky and coworkers [12,13] have used photoelectron spectra to investigate the energetics of iodide ions hydrated with up to 15 water molecules.
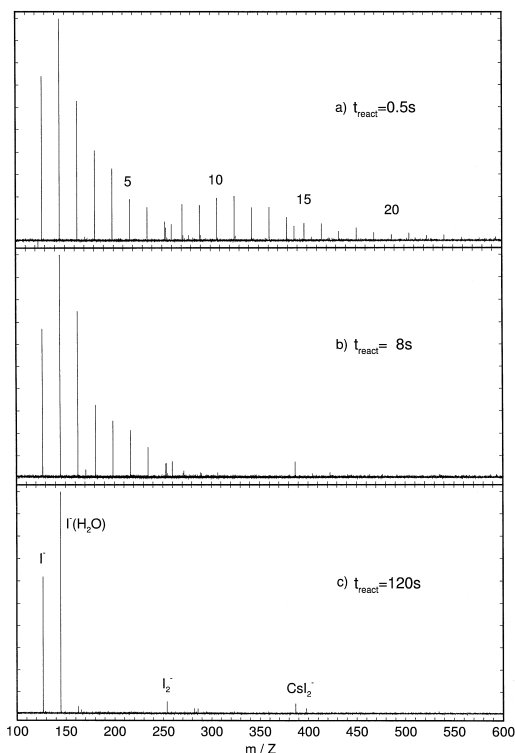

Fig. 2. Mass spectra showing the fragmentation of $I^-(H_2O)_n$ clusters $n = 0-25$, induced by IR background radiation at a pressure of about 6×10^{-10} mbar in the cell region after variable reaction delays.
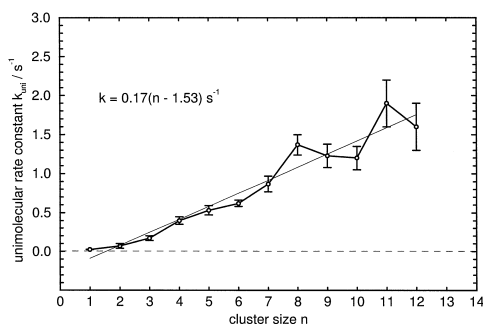
Fig. 3. Unimolecular rate constants of $I^-(H_2O)_n$, $n = 1$–12, determined for each size separately by fitting the initial decay. The solid line represents a linear regression with the equation $k = 0.17(n - 1.53)$ s^{-1}.

From their spectra they calculated the electrostatic stabilization energies E_{stab}, which is the difference between the vertical photodetachment energy of the ion solvated in the cluster and the electron affinity of the bare ion. They observed that for clusters with $n > 6$ the increase of the vertical stabilization energies E_{stab} levels off. This was considered to be a strong indication that iodine forms a first solvation shell with six water molecules. Based on the experimental data of Cheshnovsky and coworkers and their conclusion, one could expect the iodide water clusters to exhibit an enhanced stability due to the closed-shell structure with six water molecules. Our measured rate constants do not show, within the error of the experiments, significant discontinuity and departure from the linear regression line at $n = 6$. This is quite surprising as one might expect that on the timescale of the ICR study, which is typically six orders of magnitude longer than in ion beam experiments, the $I^-(H_2O)_n$ species should come closer to their thermodynamic minimum structure and energetically favoured structures should become even more apparent.

3.2. Reaction with HCl

In addition to fragmentation we have also investigated the reaction of the $I^-(H_2O)_n$ cluster ions with hydrochloric acid (pressure in the cell region: $\sim 1 \times 10^{-8}$ mbar). The reactions proceed by a series of fragmentation and ligand exchange processes. The analysis of the data is complicated by the fact that

particularly in the initial phase (Fig. 4a) there is a competition between collisionally as well as radiation induced fragmentation on the one hand and dissolving of HCl in the cluster on the other:

$$I^-(H_2O)_n + HCl \rightarrow I^-(H_2O)_{n-x} + HCl + xH_2O \tag{1}$$

$$\rightarrow I^-(H_2O)_{n-y}(HCl) + yH_2O \tag{2}$$
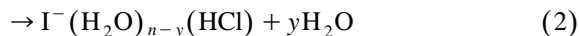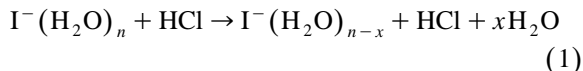
At longer reaction delays (Fig. 4b), the HCl-containing clusters undergo a series of further ligand switching reactions:

$$I^-(H_2O)_n(HCl)_k + HCl$$
$$\rightarrow I^-(H_2O)_{n-x}(HCl)_{k+1} + xH_2O. \tag{3}$$
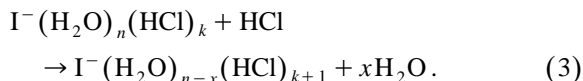
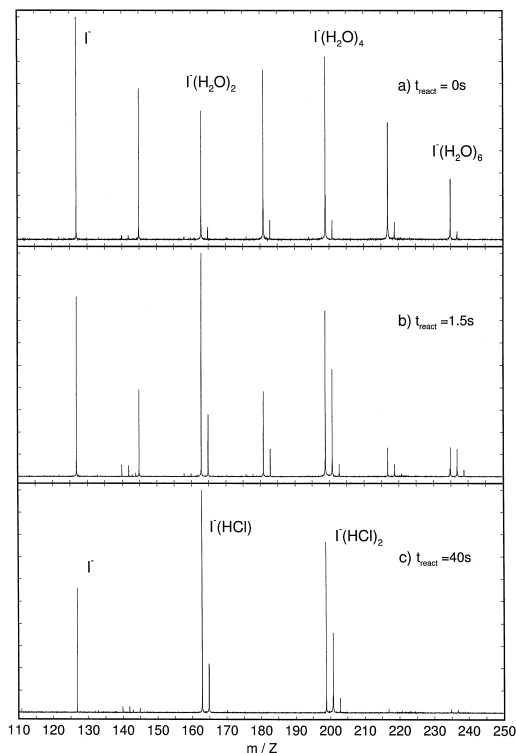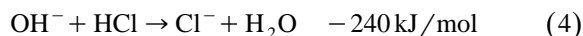After a sufficiently long time all the water is eliminated and the terminal products are essentially I^-

Fig. 4. The reaction of $I^-(H_2O)_n$, $n = 0$–7, with hydrochloric acid at a pressure of about 10^{-8} mbar in the cell region proceed by a series of fragmentation and ligand exchange processes. After a reaction delay of 40 s, all the water is eliminated and the terminal products are essentially I^- anions solvated with HCl molecules.
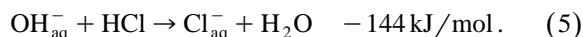
anions solvated with HCl molecules, $I^-(HCl)_k$, $k = 0-2$.

We have recently investigated the reactions of gaseous hydrochloric acid with a variety of singly charged ionic clusters solvated with up to 100 water molecules [21,28–31]. In these experiments both cationic (H^+, Mg^+, Al^+) and anionic (OH^-, O^-) cluster species were investigated. This work has revealed that depending on the cluster charge, the mechanism and the driving force of the process are different, as is also its outcome. The reactions of the cationic clusters are driven by the large 75 kJ mol^{-1} enthalpy of the solution of hydrochloric acid. The HCl molecules ligand-exchange readily with sufficiently large hydrated clusters and dissolve with ionization in the cluster. Thus for hydrated proton $H^+(H_2O)_n$ species it was found that clusters with $n \geq 10$ water ligands can dissolve one and those with $n \geq 13$ water molecules, two HCl molecules. Smaller clusters, which contain not enough water ligands to solvate the H^+ and Cl^- ions do not ligand-exchange. Conversely, when larger clusters containing HCl are allowed to fragment, when the above solubility limits are reached, the HCl solute rather than the water ligand is evaporated.

The driving force of the anionic cluster reactions is the large electron affinity of chlorine (348.3 kJ mol^{-1}). In the first reaction step the ionic core of the cluster is replaced by a chlorine-containing species. Thus in reactions of hydrated hydroxyl anions, $OH^-(H_2O)_n$, a proton transfer from HCl to the OH^- anion $(EA = 176.4$ kJ mol$^{-1})$ takes place, forming a solvated chloride anion. This process is naturally strongly exothermic, with the amount of heat released depending on the size of the cluster. It can be estimated from the available thermodynamic data (heat of formations were taken from Ref. [32]): [1] no hydration $(n = 0)$:

$$OH^- + HCl \rightarrow Cl^- + H_2O \quad -240 \, kJ/mol \qquad (4)$$

bulk hydration $(n = \infty)$:

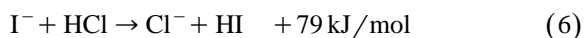$$OH^-_{aq} + HCl \rightarrow Cl^-_{aq} + H_2O \quad -144 \, kJ/mol. \qquad (5)$$

The heat released in this proton transfer results in the evaporation of one or several water ligands. In our

previous study with size-selected water cluster $OH^-(H_2O)_n$ anions we could establish that a dissolution of HCl in the cluster was typically followed by an evaporation of one or two water molecules [6]. This is in rough agreement with the above numbers and with the bulk heat of sublimation of water of about 50 kJ mol^{-1}. In subsequent collisions gradual fragmentation and ligand exchange of the remaining water molecules for HCl take place, resulting in the $Cl^-(HCl)_n$ final product.

The reactions of $I^-(H_2O)_n$ with hydrochloric acid are analogous to those of the other anionic species. One observes fragmentation and ligand exchange reactions, as seen in Fig. 4. However, even although the electron affinity of chlorine (348.3 kJ mol^{-1}) is higher than the electron affinity of iodine (295.2 kJ mol^{-1}), no shift of the charge to form Cl^- and evaporation of HI from the cluster can be detected. This can again be understood based on thermodynamic considerations and on the considerably higher binding energy of HCl (431 kJ mol^{-1}) as compared with HI (299 kJ mol^{-1}).

By means of the thermodynamic data available one can obtain for the two limiting cases: no hydration $(n = 0)$:

$$I^- + HCl \rightarrow Cl^- + HI \quad +79 \, kJ/mol \qquad (6)$$

bulk hydration $(n = \infty)$:

$$I^-_{aq} + HCl \rightarrow Cl^-_{aq} + HI \quad +1 \, kJ/mol. \qquad (7)$$

Chloride does not exchange for iodide since this reaction appears to be endoergic irrespective of the degree of hydration. While in the case of bulk hydration (7), the difference is smaller than the combined uncertainties of the thermochemical data entering the computation (several kJ/mol) it seems unlikely, however, that the error could be sufficiently large to make the reaction exoergic within the limited range of hydration $(n \leqslant 7)$ studied in the present study.

4. Conclusion

Hydrated halide ions $I^-(H_2O)_n$, $n = 0-25$, were produced by laser vaporization. Fragmentation of the clusters, caused by absorption of black-body radiation from the walls of the vacuum chamber, shows an overall $k \sim n$ dependence. Gas-phase chemical reactions are observed with hydrochloric acid. They

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[1] Bulk-phase hydration enthalpies of ions were taken from Ref. [33].

proceed by a series of fragmentation and ligand exchange reactions and result in the final $I^-(HCl)_n$ ions, $n = 0–2$.

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