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Birch reduction of chlorobenzene in gas-phase hydrated electrons

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Dedicated to Eugen Illenberger on the occasion of his 65th birthday.

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ABSTRACT

Reactions of gas-phase hydrated electrons $(H_2O)_n^-$, $n = 30$–65, with chlorobenzene are investigated by Fourier transform ion cyclotron resonance mass spectrometry. The clusters lose water molecules via collision and black-body radiation induced dissociation. In addition, chemical reactions with chlorobenzene lead to formation of $Cl^-(H_2O)_n$ and $OH^-(H_2O)_n$. While the former product is well-known from pulsed radiolysis studies in the bulk, the latter is observed for the first time in gas-phase clusters. It is indicative of a Birch reduction of the aromatic ring, leading to formation of a chloro-cyclohexadienyl radical $C_6H_6Cl^\bullet$.

1. Introduction

The conceptually simplest charge transfer reaction is electron attachment in the gas phase. Illenberger, Märk, and Scheier have recently published a series of results revealing an unexpected and intriguing site-selective activation of biomolecules, which can be controlled by the kinetic energy of the free electrons [1–5]. Electrons in aqueous environment, so-called hydrated electrons, have been investigated since their discovery [6] by pulsed radiolysis, and a large data base regarding their chemical reactions is available [7].

In the gas phase, the spectroscopic properties of hydrated electrons $(H_2O)_n^-$, with $n < 100$, are currently investigated by several groups [8–12]. In particular the debate whether a transition from surface to internal solvation is occurring in this size regime is ongoing [13]. Viggiano and Johnson have investigated the reactivity of hydrated electrons towards a series of small molecules in flow reactors, mostly observing charge transfer processes [14,15].

Hydrated electrons in bulk water e_{aq}^- are short lived due to a variety of recombination reactions [7]. In the gas phase, $(H_2O)_n^-$, $n > 14$, can be trapped in an FT-ICR mass spectrometer, and their lifetime seems to be limited only by their gradual loss of water molecules [16,17]. For $n < 30$, electron detachment competes with water loss, with a strong, non-monotonic size dependence. The longevity offers a unique opportunity to study the chemistry of hydrated electrons in an idealized manner. When a volatile reactant is introduced into the ultra-high vacuum region of the FT-ICR instrument, individual molecules collide with the hydrated electrons. Ultra-high resolution mass spectrometry allows for monitoring the reaction kinetics and identifying the reaction products quantitatively. For these reasons, FT-ICR mass spectrometry has been utilized in our group to investigate the gas-phase reactivity of hydrated electrons for several years [18–23].

Particularly interesting is the observation of a birch-like reduction in the reaction of $(H_2O)_n^-$ with acetonitrile [18]. Upon collision of a hydrated electron with CH_3CN, formation of $OH^-(H_2O)_n$ is observed. From thermochemical arguments it is unambiguously inferred that a neutral radical, either CH_3CHN or CH_3CNH, is formed. Highly specialized microorganisms contain dearomatizing ring reductases to perform the Birch reduction of aromatic rings in aqueous environment. The most difficult step in these reactions is the first electron transfer, which destroys the aromaticity [24–26]. In the present manuscript, we report our results of the reactions of hydrated electrons $(H_2O)_n^-$ with chlorobenzene, which provide evidence that these systems are capable of initiating the Birch reduction of aromatic rings.

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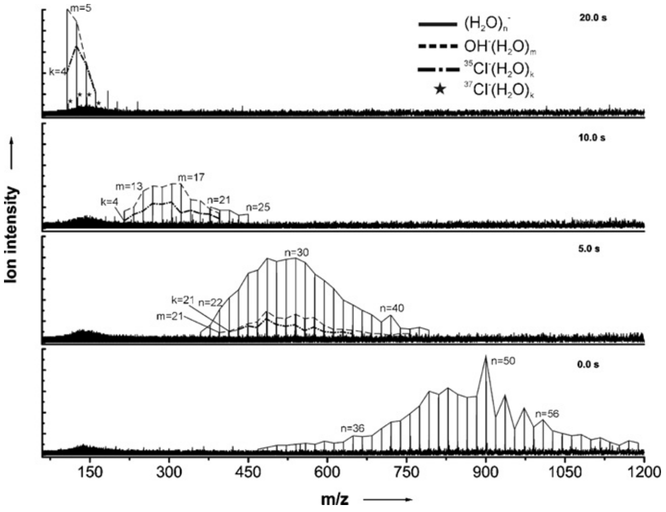


Fig. 1. Selected mass spectra for the reaction of $(H_2O)_n^-$, $n = 30–65$, with C_6H_5Cl at a pressure of 7.7×10^{-9} mbar, after 0 s, 5 s, 10 s, and 20 s. For $n < 30$, $(H_2O)_n^-$ detach electrons in parallel to the black-body radiation and collision induced evaporation of water molecules, explaining the poor signal-to-noise ratio in the 10 s spectrum.

2. Experimental

The experiments were performed on a modified Bruker Spectrospin CMS47X mass spectrometer, equipped with an APEX III data station, a Bruker Infinity cell, and an external laser vaporization source as described in detail before [16,27,28]. Hydrated electrons were produced by laser vaporization [29,30] of a solid zinc target disk (Aldrich, 99.9% +) by a frequency-doubled pulsed Nd:YAG laser, wavelength 532 nm. The metal plasma was entrained in a 50 μs pulse of helium at a backing pressure of 20 bar, which has been seeded with water vapor at a temperature of 20 °C, followed by supersonic expansion into high vacuum, which results in the formation of $(H_2O)_n^-$. The clusters were transferred by electrostatic lenses through several stages of differential pumping into the high-field region of the superconducting magnet and stored inside the ICR cell. 20 cycles of laser vaporization were accumulated and 50 mass spectra averaged to reach an acceptable signal-to-noise level. The reaction gas is introduced to the cell region by a needle valve, raising the pressure from below 10^{-10} mbar to a constant value of 7.7×10^{-9} mbar. Here, the pressure readout was scaled with the polarizability of chlorobenzene. Liquid chlorobenzene (Aldrich, >99%) was degassed by three pump-freeze-thaw cycles. To monitor the reaction, mass spectra were recorded after varying reaction delays. The reproducibility of the results was tested over the course of 2 weeks, and with different reactant gas pressures. The ratio of the products never changed. With very high reactant pressures, the products were present with more than 50% abundance from the beginning, so we could rule out that e.g., the $OH^-(H_2O)_n$ product comes from the source. Chlorobenzene decomposes at room temperature. When the colour had turned slightly yellow, typically after 24 h at room temperature and ambient light, additional product peaks appeared, which vanished after introduction of fresh sample.

3. Results and discussion

Fig. 1 shows mass spectra of the reaction of $(H_2O)_n^-$, $n = 30–65$, with C_6H_5Cl at a pressure of 7.7×10^{-9} mbar after 0 s, 5 s, 10 s and 20 s reaction delay. After 5 s, only about 30% of the clusters have reacted, which indicates that the reaction proceeds significantly below collision rate. The mass spectra are shifted towards lower masses with increasing reaction delay due to collision and black-body radiation induced dissociation. After 10 s, the clusters are in a size region where the electron is detached [16], leaving only the reaction products, which continue to fragment. Slow formation of $Cl^-(H_2O)_n$ and $OH^-(H_2O)_n$ is observed, accompanied by collision and black-body radiation induced [31–36] dissociation. After 20 s, almost all water molecules have evaporated.

Fig. 2 shows a zoom on the peak group around $(H_2O)_{26}^-$ after a reaction delay of 5.0 s. The hydrogen transfer product $OH^-(H_2O)_{25}$ indicates that the Birch reduction of chlorobenzene towards C_6H_6Cl has taken place. It is clearly resolved from the isobaric peak of $^{35}Cl^-(H_2O)_{24}$. The assignment is confirmed by the presence of the $^{37}Cl^-(H_2O)_{24}$ isotope peak. We can thus summarize the results with the following reactions:

$$(H_2O)_n^- + C_6H_5Cl \rightarrow Cl^-(H_2O)_{n-m} + C_6H_5^{\bullet} + mH_2O \tag{1}$$

$$(H_2O)_n^- + C_6H_5Cl \rightarrow OH^-(H_2O)_{n-p-1} + C_6H_6Cl^{\bullet} + pH_2O \tag{2}$$

$$(H_2O)_n^- + C_6H_5Cl \rightarrow (H_2O)_{n-1}^- + C_6H_5Cl + H_2O \tag{3}$$

$$(H_2O)_n^- + qh\nu_{IR} \rightarrow (H_2O)_{n-1}^- + H_2O \tag{4}$$

The isobaric overlap of the $^{35}Cl^-(H_2O)_{n-m}$ and $OH^-(H_2O)_{n-p-1}$ products did not allow us to determine the values of m and p in a quantitative way, as we did on earlier occasions [22,23]. However, from literature thermochemistry for reactions (5)–(8) [37–39] we can calculate the enthalpy of the equivalent of reaction (1) in solution, reaction (9), to $\Delta H(9) = -141 \pm 9$ kJ/mol. With the previously assumed evaporation enthalpy of 38 kJ/mol [22,23] for a water molecule from the cluster, this corresponds to the loss of $m = 3.7$ H_2O in (1).

$$C_6H_5Cl(g) \rightarrow C_6H_5(g) + Cl(g) \quad \Delta H = +406 \pm 8 \text{ kJ/mol [37]} \tag{5}$$

$$Cl(g) + e^-(g) \rightarrow Cl^-(g) \quad \Delta H = -354.81 \text{ kJ/mol [38]} \tag{6}$$

$$Cl^-(g) \rightarrow Cl^-(aq) \quad \Delta H = -364 \text{ kJ/mol [38]} \tag{7}$$

$$e^-(aq) \rightarrow e^-(g) \quad \Delta H = +171.9 \pm 3.8 \text{ kJ/mol [39]} \tag{8}$$

$$C_6H_5Cl(g) + e^-(aq) \rightarrow Cl^-(aq) + C_6H_5(g) \quad \Delta H = -141 \pm 9 \text{ kJ/mol} \tag{9}$$

Not all data are available for the thermochemistry of reaction (2), but we can calculate the enthalpy to release a hydrogen atom from a solution phase solvated electron to the gas-phase, reaction (14), by combining reactions (8), (10)–(13), to yield $\Delta H(14) = +74.64$ kJ/mol.

$$H_2O(aq) \rightarrow H_2O(g) \quad \Delta H = +44{,}01 \text{ kJ/mol [38]} \tag{10}$$

$$H_2O(g) \rightarrow OH(g) + H(g) \quad \Delta H = +498{,}81 \text{ kJ/mol [38]} \tag{11}$$

$$OH(g) + e^-(g) \rightarrow OH^-(g) \quad \Delta H = -180{,}08 \text{ kJ/mol [38]} \tag{12}$$

$$OH^-(g) \rightarrow OH^-(aq) \quad \Delta H = -460 \text{ kJ/mol [38]} \tag{13}$$

$$e^-(aq) \rightarrow e^-(g) \quad \Delta H = +171.9 \pm 3.8 \text{ kJ/mol [39]} \tag{8}$$

$$e^-(aq) + H_2O(aq) \rightarrow OH^-(aq) + H(g) \quad \Delta H = +74.64 \text{ kJ/mol} \tag{14}$$

G3 calculations reveal that addition of H to C_6H_5Cl in the gas phase is most favorable in the ortho position, reaction (15), with $\Delta H(15) = -124{,}5$ kJ/mol. Combination of reactions (14) and (15) shows that reaction (2) releases $\Delta H(16) = -49.9$ kJ/mol if conducted

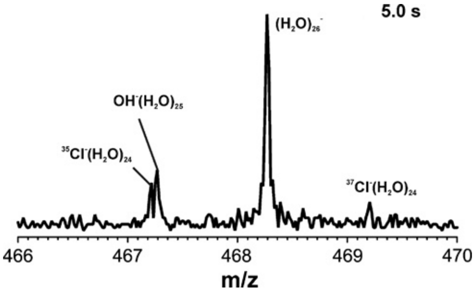


Fig. 2. Peak group around $(H_2O)_{26}^-$ after a reaction delay of 5.0 s. The hydrogen transfer product $OH^-(H_2O)_{25}$ indicates that the Birch reduction of chlorobenzene towards C_6H_6Cl has taken place. It is resolved from the isobaric peak of $^{35}Cl^-(H_2O)_{24}$.

with a solution-phase hydrated electron, or $p = 1.3 H_2O$ in (2).

$$e^-(aq) + H_2O(aq) \rightarrow OH^-(aq) + H(g) \quad \Delta H = +74,6\ \text{kJ/mol} \qquad (14)$$

$$C_6H_5Cl(g) + H(g) \rightarrow o\text{-}C_6H_6Cl(g) \quad \Delta H = -124,5\ \text{kJ/mol} \qquad (15)$$

$$C_6H_5Cl(g) + e^-(aq) \rightarrow OH^-(aq) + o\text{-}C_6H_6Cl(g) \quad \Delta H = -49,9\ \text{kJ/mol} \qquad (16)$$

These thermochemical values are in line with the experimental observation that both products are formed with quite similar cluster size distributions, with the intensity of the $Cl^-(H_2O)_{n-m}$ product shifted to slightly lower masses relative to $OH^-(H_2O)_{n-p-1}$, because $2.4 H_2O$ more are released upon Cl^- formation. An exactly parallel intensity pattern of the products would correspond to a difference of $2H_2O$.

The most intense peak group after 20 s is displayed in Fig. 3. Due to the shifted mass range, the two isobaric peaks $OH^-(H_2O)_5$ and $^{35}Cl^-(H_2O)_4$ are now well separated. The experimental mass difference of measured 0.0446 u agrees to 0.1% with the expected 0.0445 u. Overall, the 20 s spectrum indicates that Cl^- abstraction and Birch reduction occur with equal probability. Secondary reactions are not observed.

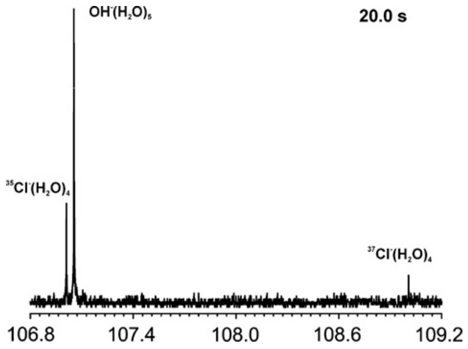
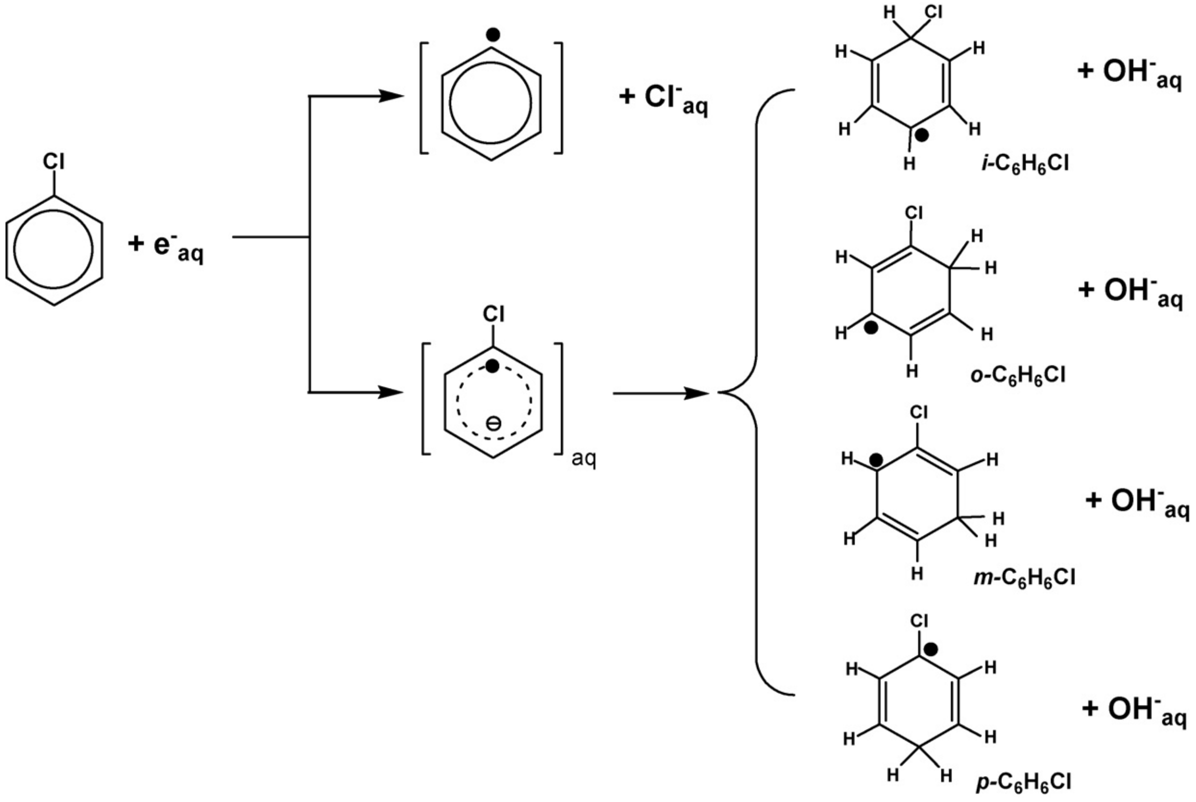


Fig. 3. Most intense peak group after 20 s. $OH^-(H_2O)_5$ and $^{35}Cl^-(H_2O)_4$ are two distinct peaks in this mass range. $^{37}Cl^-(H_2O)_4$ is present corresponding to the natural abundance of the heavier chlorine isotope.

Our previous results with benzonitrile revealed that it is taken up by the cluster, forming a solvated $C_6H_5CN^-$ radical anion [20], in agreement with the results from pulse radiolysis [40,41]. For chlorobenzene, pulse radiolysis studies report a quantitative elimination of chloride in reactions with hydrated electrons [42–44]. In studies where $H^\bullet$ atoms are selectively prepared, however, those are added to form a cyclohexadienyl radical [44,45], which is equivalent to a combination of the first two steps of the Birch reduction. Scheme 1 summarizes the reaction mechanism and illustrates the four possible hydrogen addition products.

Our gas-phase clusters seem to be able to behave both like bulk hydrated electrons or hydrogen radicals, with equal probability in



Scheme 1. Mechanism of the reaction of chlorobenzene with hydrated electrons in the gas phase, abbreviated as e_{aq}^- H addition is thermochemically most favorable in the ortho position.

the reaction with chlorobenzene. Reaction (1) corresponds fully to the established bulk behaviour and is in perfect agreement with chemical intuition. It is equally straightforward to rationalize the hydrogen addition in reaction (2) as previously suggested for acetonitrile [18]. Upon uptake of the neutral reactant by the cluster, a radical anion $C_6H_5Cl^{\bullet-}$ is formed, followed by proton transfer from the neutral hydration shell to yield the neutral $C_6H_6Cl^{\bullet}$ and a hydrated hydroxide ion $OH^-(H_2O)_n$. The cyclohexadienyl radical is the most weakly bound entity, thus it is preferentially evaporated from the cluster.

The question remains why gas-phase hydrated electrons behave differently from their counterparts in bulk aqueous solution. At this time, we can only speculate. The higher temperature of the bulk solution, i.e., the higher amount of energy available in the reaction coordinate, may favor Cl^- elimination.

4. Conclusions

The formation of $OH^-(H_2O)_n$ in the reaction of hydrated electrons with chlorobenzene is indicative of a Birch reduction of the aromatic system in a small water cluster. In bulk solution, reactions of this type have to be performed in liquid ammonia, while the finite environment of gas-phase clusters makes the reaction feasible in aqueous media. It is fascinating to imagine that nature utilizes confined water clusters in enzymes to beat the upper limit of aqueous redox potentials, which is necessary for the Birch reduction.

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