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Review

Free electrons, the simplest radicals of them all: chemistry of aqueous electrons as studied by mass spectrometry

O. Petru Balaj, Chi-Kit Siu, Iulia Balteanu, Martin K. Beyer*, Vladimir E. Bondybey

Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

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Abstract

In the present manuscript we review the chemistry of aqueous electrons, as studied by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. FT-ICR studies of the $(H_2O)_n^-$ reactions have the advantage that compared with bulk solutions the electrons exhibit long lifetimes, and impurity effects can be completely eliminated. The review demonstrates that aqueous electrons, the simplest chemical reagents, exhibit a multifaceted chemistry, and may provide new insights into the aqueous chemistry of neutral and anionic radicals. We show that the cluster reactions can be loosely classified into several categories, and give representative examples for each of them.

Keywords: Hydrated electrons; Solvated electrons; Nanodroplets; Gas-phase reactions; Radical ions

Contents

1. Introduction

Atoms are bound together in molecules by electrostatic forces. A molecular bond forms, when the attractive forces between the atomic nuclei and the shared electrons prevail over the repulsive forces between the positively charged nu-

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* Corresponding author. Fax: +49 89 289 13417.
E-mail addresses: beyer@ch.tum.de (M.K. Beyer), bondybey@ch.tum.de (V.E. Bondybey).

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clei. All chemical reactions therefore involve a rearrangement of electrons, and in this sense, the electron itself can be considered the simplest chemical reactant. Production of an electron typically requires an appreciable amount of energy, and free electrons in the gas phase therefore occur only in environments where large amounts of energy are available, such as flames, discharges, or plasmas. On the other hand, producing an electron in the condensed phase, where it is intimately solvated by surrounding molecules is surprisingly easy. A first clear, relevant observation of this fact in fact dates back to the early days of modern chemistry, and to the beginning of the 19th century.

Already around 1810, Humphry Davy noted that an intense blue color appeared when alkali metals were exposed to ammonia. Subsequent studies, among others by Weyl [1], established that the blue solutions behaved like electrolytes, with high electric conductivity and magnetic susceptibility, and became bronze colored and metallic in appearance at higher concentrations. Almost exactly a century after Davy's discovery, Kraus suggested that the metals are ionized in the ammonia solutions, resulting in a metal cation, and a free electron [2]. This process which requires some 5–6 eV in the gas phase proceeds in the ammonia solution spontaneously and exothermically, with the energy required for the ionization being more than compensated by the combined solvation energies of the metal cation and of the electron.

A molecule of water, undoubtedly the most important solvent, has an even higher dipole moment (1.854 D) than ammonia (1.471 D), is capable of stronger hydrogen bonding, and might therefore be expected to be even more effective in promoting the metal ionization. In spite of that, more than an additional half century has elapsed before similar solvated electrons could be generated and observed in water [3–5]. A solvated electron is highly reactive, and can be destroyed by a variety of reactions with impurities, or with the solvent itself [6]. In ammonia, the reaction with the solvent resulting in amide formation and the development of hydrogen is hindered and quite slow. Water, however, even when quite pure, is partially ionized, $H_2O \rightarrow H^+ + OH^-$, so that free electrons can efficiently recombine with the protons, greatly facilitating the solvent reduction and formation of hydrogen atoms, which in turn recombine to form molecular hydrogen.

The problem thus does not lie in the difficulty of generating the hydrated electrons, but in the efficient processes leading to their destruction. They can, in fact, be produced by a wide variety of methods, including direct injection of energetic electrons into the solvent [3–5], photoionization of water itself [7,8], or of a suitable precursor [9,10] by UV radiation, and they also form, albeit transiently by the interaction of water with alkali metal surfaces [11]. Although they are easily produced by pulsed radiolysis of aqueous solutions and other methods, they have only very short, pH dependent lifetimes of less than 1 ms [9]. The appreciable volume increase which accompanies the injection of electrons into liquid water, motivated the development of the so called "cavity" model of solvated electrons [12]. This simple treatment of such a hydrated electron as a particle in a three-dimensional box leads to an s-type ground state, with an excited triply degenerate p-type excited state. It is the fully allowed s–p excitation in this model which gives the hydrated electrons their blue color, and the strong broad absorption in the red, with a maximum around 720 nm [8,13,14].

Unlike in bulk liquid, water autoionization does not occur in finite clusters, and therefore no protons, or H_3O^+ ions, limiting the free electron lifetimes should be present. Haberland and coworkers have demonstrated, that gas phase hydrated electrons, that is small negatively charged water clusters $(H_2O)_n{}^-$ can be produced [15–17], and since then these species have been quite extensively studied, both experimentally [18–23] and theoretically [24–34]. A more extensive account of these works is given in a previous publication [21]. Most of these studies concentrated upon the physical properties of the water clusters, upon the question of their formation [35–37], stability [21,38] and electronic and geometric structure [18–20]. The clusters or "nandodroplets" thus provide a suitable medium, free of interference by impurities, where the lifetime of the free electrons is not limited by the presence of protons. This then permits convenient studies of the chemistry of these interesting reactants, as already exemplified by a series of investigations both in our laboratory [23,39,40] and earlier by Johnson and coworkers [41,42]. These studies of hydrated electron reactions and chemistry form the subject of the present review.

2. Generation of hydrated electrons $(H_2O)_n{}^-$

As noted above, hydrated electrons $(H_2O)_n{}^-$ can be generated by a variety of methods. The studies by Haberland and coworkers have employed electrons produced by UV photons [15–17]. One can also first produce neutral water clusters in a supersonic expansion, and subsequently attach low energy electrons [35–37]. Quite recently we have demonstrated, that a versatile laser vaporization source developed in our laboratory can be used as a very efficient, clean source of hydrated electrons [21,23]. This source which combines supersonic expansion with pulsed laser vaporization of a solid metal sample can generate metal cations and cationic clusters, as well as electrons, anions and anionic clusters. When one employs a metal sample with negative electron affinity, such as zinc, the metal anions and anion clusters can effectively be eliminated [23]. When a small amount of water vapor is then introduced into the high pressure carrier gas, usually helium, pure hydrated electron clusters are produced.

These are then extracted from the beam, and guided along the magnetic field axis, through several stages of differential pumping from the source chamber into the high vacuum region of the ICR cell. The specific distribution of the clusters depends on the exact source conditions, the stagnation pressure of the carrier gas, on the water vapor partial pressure, and in particular on the relative timing between the opening of the pulsed valve controlling the gas expansion and the vaporization laser pulse. Typically, $(H_2O)_n{}^-$ clusters ranging in size from n = 15 to about 100 can be produced. At the high end, the distribution is limited by the rapid fragmentation and short lifetime of the large clusters due to absorption of the black-body ambient infrared radiation. Clusters with $n < 13$, on the other hand, have very short lifetimes due to a rapid electron detachment process. These can be generated and studied on the shorter timescale of a molecular beam experiment, but do not survive sufficiently long to be detected in the ICR cell, which requires a lifetime of at least 100 ms due to the detection process.

3. Cluster stability and fragmentation

Before discussing the $(H_2O)_n{}^-$ cluster reactions and collisional fragmentation, it is necessary to note, that even in the total absence of collisions they gradually disappear from the ICR trap, due mainly to the absorption of black-body infrared radiation. The clusters are held together by hydrogen bonds between the water molecules, and are not stable at room temperature. In the ICR trap they can survive, because their temperature upon leaving the supersonic expansion is quite low. The water molecules are, however, in particular when hydrogen bonded, excellent infrared absorbers, and are continuously exposed to the black-body radiation of the room temperature apparatus walls. Absorption of the infrared photons steadily supplies energy, and leads to gradual evaporation of the water ligands [21,43–50]. The cluster temperature is thus controlled by the competition between evaporative cooling and radiative heating. This process will only come to a halt when the clusters reach the ambient temperature of around 300 K, that is when they are in thermal equilibrium with the environment. The hydrated ions thus eventually reach some minimum size, at which the available thermal energy content is no longer sufficient to break the bonds and cause unimolecular decomposition [45]. They become stable at room temperature on the time scale of the ICR experiment—usually in the range of many seconds. Thus, for instance for hydrated protons, the final, effectively stable product of fragmentation is $H^+(H_2O)_4$, perhaps better formulated as hydrated hydroxonium, $(H_3O^+)(H_2O)_3$, which then survives in the absence of collisions for seconds or even minutes [46].

Unlike the compact, effectively point-like proton, the diffuse charge of the electrons binds much more tenuously to the water ligands. In the case of the hydrated electron clusters, there are therefore two competing processes which contribute to the loss of a cluster of a given size. The cluster can either "evaporate" a water ligand, or it can detach the electron, and both processes are actually experimentally observed [21].

A detailed study in our laboratory has shown [21], that for clusters above about n = 30 the latter process is negligible, and ligand loss is the dominant process. Fig. 1 shows the rate constants of the two processes together with their branching ratio. For $16 < n < 32$, one observes a wild fluctuation in the relative importance of the two processes, with some species almost exclusively fragmenting with the loss of ligand, while for other sizes detachment of the electron making a significant contribution to the overall cluster decay. The electron detachment is the only process detectable for $n < 17$, and this is reflected in the drastic drop in intensity in the initial mass spectra below n = 17, with the smallest cluster observed only in traces being n = 13. We have interpreted the fact, that experimentally the larger clusters lose a ligand rather than the electron as an effect of entropy [21,22]. In essence, while most of the internal energy of the cluster would have to be concentrated in the vibrational modes localized around the solvated electron to enable it to exit the cluster, any of the n water ligands can evaporate, making the latter process statistically more probable.

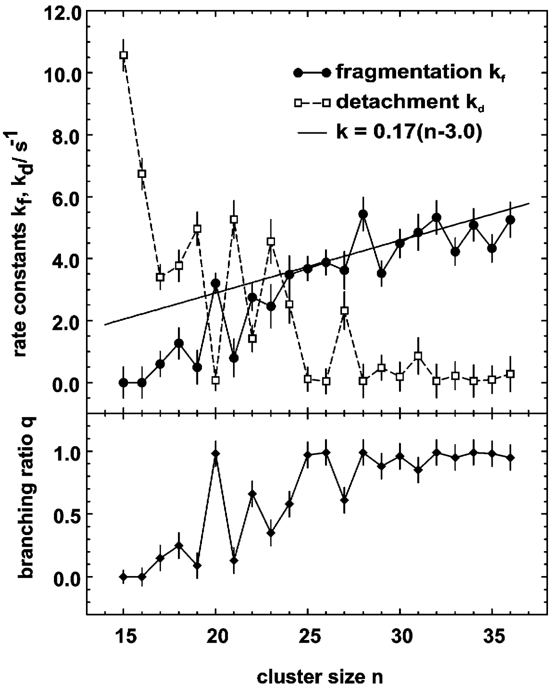

Fig. 1. Fragmentation k_f and detachment k_d rate constants and branching ratio q $k_f/(k_f + k_d)$ of the black-body radiation induced decay of size selected hydrated electron clusters $(H_2O)_n{}^-$ as a function of cluster size. The branching ratio increases from 0 to 1, but pronounced odd–even oscillations are observed around n = 20. While the larger clusters exclusively fragment, the electron detachment becomes more important with decreasing cluster size, and is the only process detectable for clusters containing less than 17 water molecules. The solid line shows the expected rate constant based on the linear dependence of the fragmentation rate constants on the cluster size [45,46]. Reprinted with permission from ref. [21]. © 2001 American Institute of Physics.

It may be noted, that the smaller clusters below n =13 can be detected in experiments where the time scale is shorter than the >100 ms for ICR studies. For instance, in molecular beams, clusters with $n \geq 6$ are routinely observed, as well as the dipole bound anion of the water dimer. Recently, also the previously "missing" n = 3–5 clusters were observed [51].

4. Reactions of solvated electrons

As noted above, the solvated electron clusters provide an interesting medium for studying reactions of aqueous electrons. These simple reactants exhibit a very multifaceted chemistry with a surprising variety of their chemical reactions, which can be crudely classified into at least the following four categories:

(a) Collisional activation: Nonreactive, nonpolar species, with low or negative electron affinity, for example rare gases like He or Ar, or stable molecules like carbon monoxide or ethylene, do not react at all with the solvated electron. The only process observed is a collision-induced increase of the fragmentation rate of the cluster.
(b) Ligand exchange: Polar molecules, which similar to water capable of forming strong hydrogen bonds and hydrogen bonded networks, such as methanol or other alcohols, react with the clusters by ligand exchange, replacing gradually a part or possibly all of the aqueous shell by the reactant molecules.
(c) Core exchange: Species characterized by appreciable electron affinity in solution can simply attach the electron, forming a negative ion, and replacing thus the ionic core of the cluster.
(d) Rearrangement of covalent bonds: Finally, a true chemical reaction, that is a process where existing covalent bonds are broken or new ones are formed may occur.

Below we will give a brief review of the previous studies, and include some previously unpublished results from our laboratory as well as speculations on the outcome of future experiments. Table 1 summarizes the reactions for which experimental data are available to date.

4.1. Collisional activation (a)

In view of reactivity studies with a collision gas introduced into the ICR cell, collisional fragmentation will obviously only be significant, if its rate becomes comparable to the rate of the radiative process, that is when the time between collisions between the clusters and the reactant gas are short compared the rate of energy absorption from the black-body radiation. Typically, the studies in our laboratory are carried out at pressures of the order of 10^{-8} mbar, under conditions when only about one collision per second takes place. Under these circumstances, the effects of collisional fragmentation are small for clusters containing more than 10 water molecules, which is always the case for hydrated electrons. Collisional activation will thus lead to a small increase in the dissociation rate constants, which will usually still be dominated by black-body radiation.

Table 1
Summary of the hydrated electron cluster reactions with different molecules

Reactant	Product	Type of reaction	Final product	
			Number of water molecules n	Electron detachment
CO[a]	–	a		Yes
C_2H_4[a]	–	a		Yes
$C_6H_5CH_3$[a]	–	a		Yes
N_2[b]	–	a		Not probed
CH_3F[b]	–	a		Not probed
CH_3OH[a]	$(H_2O)_n(CH_3OH)_{1-6}{}^-$	b		Yes
O_2[b,c,d]	$O_2{}^-(H_2O)_n$	c	2	No
CO_2[b,c,d]	$CO_2{}^-(H_2O)_n$	c	2	Yes
$CO_2 + O_2$[d]	$O_2{}^-(H_2O)_n$	c	2	No
$CO_2 + C_2H_2$[a]	$CO_2{}^-(H_2O)_n$	c	2	Yes
CH_3CHO[a]	$(CH_3CHO)^-(H_2O)_n$	c	3[g]	Yes
CD_3CDO[e]	$(CD_3CDO)^-(H_2O)_n$	c	3[g]	Yes
CH_3COCH_3[a]	$(CH_3COCH_3)^-(H_2O)_n$	c	4	Yes
C_6H_5CN[a]	$(CH_3COCH_3)_{1-5}{}^-(H_2O)_n$	c	0[g]	Yes
NO[b,c]	$NO^-(H_2O)_n$	c		Not probed
N_2O[c,a]	$O^-(H_2O)_n$	d	3	No
	$OH^-(H_2O)_m$	d	3	No
CH_3CN[f]	$OH^-(H_2O)_n$	d	[g]	No
CD_3CN[e]	$OH^-(H_2O)_n$	d	[g]	No
Br_2[b]	$Br^-(H_2O)_n$	d		Not probed
CH_3Br[b]	$Br^-(H_2O)_n$	d		Not probed

[a] This work.
[b] Reference [42].
[c] Reference [41].
[d] Reference [40].
[e] Reference [39].
[f] Reference [23].
[g] Product undergoes further ligand exchange with the neutral reactant.

As an example, no reactions of the hydrated electrons with CO, toluene and C_2H_4 were observed in our laboratory, and even when the pressure was increased appreciably above what we typically use in the reactivity studies, the collisions resulted in only a marginal acceleration of the fragmentation process. Similar apparent unreactivity was reported for N_2 and CH_3F colliding with $(H_2O)_n^-$ by Johnson and coworkers [42].

4.2. Ligand exchange (b)

While one or more water ligands can be ejected when a water cluster undergoes a binary collision with a gas phase molecule or an atom, it is also possible for the collision partner to be trapped and inserted into the solvation shell.

$$(H_2O)_n^- + M \rightarrow M(H_2O)_{n-p}^- + pH_2O \qquad (1)$$

The simplest ligand exchange would obviously be replacing one water ligand by another water molecule, but since such a process leaves the mass unchanged, it cannot be seen in the mass spectrum. Obviously, one might study this process in an isotopic experiment, for instance by allowing the $(H_2O)_n^-$ clusters to collide with heavy water, D_2O. Such an experiment could in fact yield some interesting information about the rate of isotopic scrambling. In bulk water, as noted above, H^+ ions are present with about one molecule in 10^9 being spontaneously ionized, and proton transfer and isotopic scrambling are extremely rapid, so that in a mixture of H_2O and D_2O very rapidly a statistical concentration of HDO will be formed. In a finite $(H_2O)_n^-$ cluster, on the other hand, neither H^+ nor OH^- ions are present, and it would be of some interest to establish the probability of an exchange of hydrogen for deuterium in collisions with D_2O.

The water clusters are held together by a network of hydrogen bonds, and the above process will be particularly prevalent with species which also contain polar XH bonds, and which are thus capable of strong hydrogen bonding, for instance ammonia or alcohols. In the present work, we have examined the ligand exchange of the solvated electron cluster distribution (n = 35–60) with methanol, that is reaction (1) where $M = CH_3OH$. The ligand exchange proceeds with high collisional efficiency, and already at a nominal time t = 0, one can observe product peaks containing a molecule of methanol, indicating that nearly 20% of the $(H_2O)_n^-$ clusters have already reacted, as evidenced in Fig. 2. This results in a solvated electron, where besides the water molecules, there is also one methanol ligand. Obviously, such reaction can proceed further and additional water ligands—perhaps in some cases ultimately all—can be replaced by the reaction partner, and this is confirmed by the further course of the reaction with methanol. After a further 1 s reaction, the clusters with one molecule of methanol have in fact intensities higher than the unreacted water clusters, and also clusters with 2–4 methanol ligands, that is $(H_2O)_n(CH_3OH)_m^-$ with m = 2, 3 and 4 species are present. Simultaneously, the overall distribution shifts progressively towards lower values of n. After 6 s reaction one finds that the m = 0, that is pure hydrated electron clusters are basically gone, most prominent are species with m = 3 (n = 19–28), m = 2 (n = 19–28) and m = 1 (n = 20–27) are most prominent, and clusters with up to m = 6, that is six methanol molecules are observable. Beyond this point, the clusters continue to lose ligands, but interestingly, the pure hydrated clusters make a comeback. Apperently, in the fragmentation process the clusters lose methanol faster than the water ligands. After 8 s one again sees pure hydrated electrons, m = 0 (n = 20–27), clusters with one or two methanols, m = 1 (n = 18–27) and m = 2 (n = 18–28) are now most abundant, and the overall signal intensity decreases. After additional 2 s all signal disappears, and only noise is detectable, as can be seen in Fig. 2.

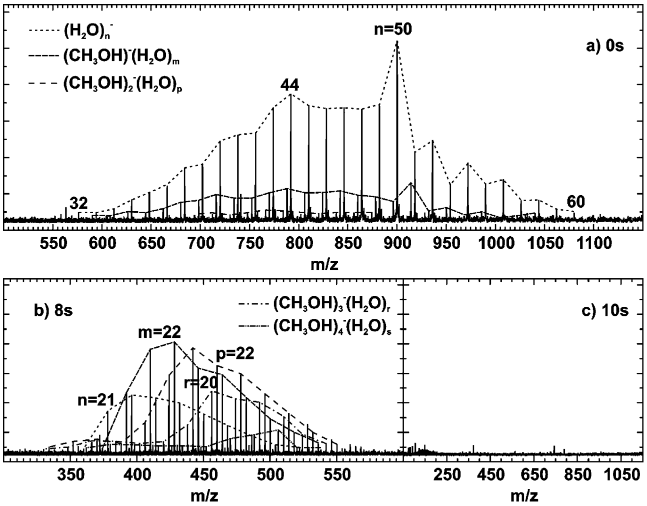

Fig. 2. Mass spectra of the reaction of $(H_2O)_n^-$ with methanol after (a) 0 s, (b) 8 s and (c) 10 s. Already at 0 s product peaks containing a molecule of methanol can be observed. After 8 s the clusters containing one, $(CH_3OH)(H_2O)_n^-$, n = 18–27, or two methanol molecules $(CH_3OH)_2(H_2O)_n^-$, n = 18–28, are most intense. After additional 2 s all signal disappears due to the electron detachment.

Methanol is similar to water in that it can form relatively strong hydrogen bonds. It is, however, less polar (μ = 1.7 D), the bonds are weaker, as also evidenced by its much higher vapor pressure, and lower boiling point of 64.6 °C. Unlike water, it also has only one polar OH bond, and can therefore not so easily form extended hydrogen bonded networks. The exchange according to Eq. (1) is probably slightly endothermic, but can occur in ambient temperature gas phase collisions. In our experiment, where essentially only methanol molecules are present in the gas phase, their collisions with the hydrated electron clusters can gradually exchange several water ligands for methanol. These will, however, most likely remain near the cluster surface, and as the fragmentation becomes dominant, will eventually also preferentially "evaporate" from the cluster. When in the course of the cluster fragmentation process the number of water ligands drops below about 25–30, the electron detachment process starts to compete with ligand loss, and before it can drop below twenty or so, all clusters will be lost. The fact that the mixed clusters seem to disappear around the comparable value of $n = 20$–25, that is with a comparable number of water ligands as the pure hydrated electrons, indicates that the methanol does not provide any additional stabilization of the electron, which is probably mainly stabilized by the water ligands.

We have not carried out the reverse of this experiment, that is exchanging the ligands of an electron solvated by pure methanol, in collisions with gas phase water molecules. Under such circumstances, if the electrons solvated by pure methanol could be produced at all, we suppose that all the ligands could be exchanged against water.

Characteristic of a ligand exchange where molecules in the solvation shell are replaced is that multiple exchanges can take place, with the probability of the process taking place on a given collision being dependent on a number of factors. The most important factor undoubtedly is the enthalpy change associated with the reaction (1). The second crucial factor is the ratio m/n, i.e., the number of new ligands m vs. the number of water molecules n in the cluster. With increasing m/n, the probability for loss of a previously exchanged ligand instead of water increases. This is evidenced by the gradual slowing and phasing out of the methanol exchange (Table 1).

4.3. *Core exchange (c)*

In the experiments discussed in the previous sections, the molecules of the reaction partner are simply traded for the water ligands of the hydrated electron. A conceptually different process involves reactions with species which bind the electron, producing a negatively charged ion. This results in the change of the ionic core of the cluster. Since the clusters contain only one solvated electron—and one ionic core—in reactions of this type one and only one of the neutral reactant molecules is taken up by the cluster.

A simple example is the reaction with O_2 [40–42]. Molecular oxygen has a $^3\Pi_g$ ground state, with a $\sigma_g^2\pi_u^4\pi_g^2$ electronic configuration, and can accommodate two additional electrons in its highest occupied degenerate antibonding π_g orbital. Accordingly, it has an appreciable electron affinity of about 2 eV. Upon collision with an $(H_2O)_n^-$ cluster, the molecular oxygen attaches the electron, forming a ground state $^2\Pi_g$ O_2^- anion. In the aqueous cluster, the water molecules will form hydrogen bonds to the negatively charged anion, which will be much more strongly hydrated than the very diffuse free electron. The electron will consequently be further stabilized in the cluster by the presence of the molecular oxygen, and this stabilization is clearly evidenced in the mass spectrometric experiment. As discussed above, when the $(H_2O)_n^-$ clusters gradually fragment and lose the solvent, the stabilization of the electron is reduced, so that eventually it is detached, with the ions completely disappearing from the ICR trap. While for pure hydrated electrons, this process is completed around $n = 15$, in the presence of a molecule of oxygen, the fragmentation proceeds further, with the total number of the anions in the trap remaining basically constant [40]. The final products of the fragmentation are the $O_2^-(H_2O)_n$, $n = 2$ and $n = 3$ species, which remain in the trap even after several minutes. The $O_2^-(H_2O)_2$ cluster neither detaches the electron, nor further fragments to $n = 1$, and is stable under the conditions of our experiment. As already noted, the electron in these clusters is tightly bound to O_2. Since the electron is intimately involved in the course of the reaction and binding the oxygen molecule, we have never observed a second O_2 to be taken up by the cluster, regardless of its size. Note that it was recently shown by infrared spectroscopy, that the first “solvation shell” of $O_2^-(H_2O)_n$ is completed with $n = 4$ [52,53].

Equally interesting, albeit somewhat different, is the case of carbon dioxide [40–42]. The linear nonpolar CO_2 owes its high stability to a closed shell structure, with a completely filled 2p π_g highest occupied molecular orbital. However, it possesses an empty, low lying antibonding orbital, also derived from the 2p electrons, which strongly favors a bent structure. Placing an additional electron in this orbital to produce the bent CO_2^- anion, which is isoelectronic with NO_2, requires a considerable energy, since unlike that of molecular oxygen, the electron affinity of ground state CO_2 is negative. On the other hand, the bent, strongly polar CO_2^- anion can form very strong hydrogen bonds to water molecules so that the reaction (2), which is strongly endothermic for $n = 0$, becomes exothermic already with $n = 1$.

$$(H_2O)_n^- + CO_2 \rightarrow CO_2^-(H_2O)_n \tag{2}$$

This was first demonstrated by the experimental observation of the mass spectrum of the $CO_2^-(H_2O)$ anion [54]. These early results were confirmed more recently by photoelectron spectroscopy [55] as well as by ab initio calculations [40,56]. The carbon dioxide anion forms a cyclic planer C_{2v} $CO_2^-(H_2O)$ anion where the two strong $O\cdots H$ hydrogen bonds stabilize the structure, and more than compensate for the negative electron affinity of CO_2. The electron is then further stabilized by additional water ligands [40]. This stabilization of the electron within the aqueous clusters is further evidenced by their behavior in the ICR experiment. In contrast with pure water solvated electrons, which are lost when the number of ligands drops below about $n = 15$, in the presence of carbon dioxide one finds again that the fragmentation proceeds further, until the final product cluster $CO_2^-(H_2O)_2$ is formed. Similar to the oxygen containing clusters, these then do not seem to fragment further to form the $n = 1$ cluster. The stabilization of the electron is, however, in this case apparently less efficient, and as the clusters are further activated by black-body radiation and collisions with the CO_2 reactant gas, they slowly detach the electron, so that the intensity gradually decreases, and after about 1 min all the ions have disappeared from the trap.

Similar to the case of oxygen, a discrete CO_2^- molecular anion is formed within the aqueous clusters, and it is the presence of the electron, which makes dissolving the carbon dioxide within the cluster possible. We have reported previously, that reacting ionic water clusters with carbon dioxide result, with the exception of collisional fragmentation, in no reaction [57]. With clusters containing metal cations such as $Mg^+(H_2O)_n$ no uptake of carbon dioxide, and no carbonate formation could be detected. It is the free electron which makes solvation of the carbon dioxide in the $(H_2O)_n^-$ cluster possible, and since only one electron is available, one and only one CO_2 molecule is taken up. The occurrence of the reaction according to Eq. (2), which appears to proceed with near unity collision efficiency has also some bearing upon the question of the cluster structure, and location of the electron within the cluster. The very efficient uptake of carbon dioxide would seem to suggest, that the electrons may not be solvated internally, but more likely localized at or near the cluster surface.

We have also carried out experiments using gas mixtures as neutral reactants [40]. In one of those experiments to study the exchange of the ionic core, CO_2 was leaked into the UHV at a relatively high partial pressure of 1.3×10^{-7} mbar, together with O_2 at a partial pressure of 5.7×10^{-8} mbar, roughly a 2:1 mixture of CO_2 and O_2. At 0.5 s reaction delay, the $(H_2O)_n^-$ distribution is completely gone, converted to $CO_2^-(H_2O)_m$ and $O_2^-(H_2O)_m$. Since CO_2 is present in twice the abundance of O_2 and CO_2 reacts three times as efficient as O_2, $CO_2^-(H_2O)_m$ predominate in the spectrum. After 3 s, $O_2^-(H_2O)_m$ have become the dominant species indicating that the core exchange has already occurred, and the additional $O_2^-(H_2O)_m$ comes from reactions with $CO_2^-(H_2O)_m$. After 10 s this process is almost complete, and only traces of $CO_2^-(H_2O)_m$, with $m \approx 10$, remain in the mass spectrum. This charge transfer from CO_2^- to O_2 was also observed in the condensed phase, with rate constants of $2.0–2.4 \times 10^{-9}\ dm^3\ mol^{-1}\ s^{-1}$ at 298 K [58,59]. Although no activation energies are reported, comparison with charge-transfer reactions with similar rate constants [59], suggests that the activation energy for the CO_2^-/O_2 reaction lies around 10 kJ/mol. This amount of energy is readily available in the large water clusters, which are continuously heated by collisions and black-body radiation.

In another experiment a 1:1 mixture of CO_2 and C_2H_4 induced the formation of $CO_2^-(H_2O)_n$ as the only product. The only contribution of ethylene is in the increase of the collision induced fragmentation, while a coupling of the CO_2^- radical anion with the carbene was not observed.

Acetone behaves similar to CO_2. After 1 s about 50% of the initial hydrated electron clusters have reacted to $(CH_3COCH_3)^-(H_2O)_n$, at an acetone pressure which is twice as high as the CO_2 pressure in the comparable experiment. For comparison, the clusters need 2 s in the case of CO_2 to achieve a 50% conversion into products. This suggests that acetone, like CO_2, reacts with collision rate with the cluster. After 7 s reaction delay, the clusters have been completely transformed into products. The $(CH_3COCH_3)^-(H_2O)_n$ ions fragment, after 28 s, to the final product, $(CH_3COCH_3)^-(H_2O)_4$. Due to the presence of a very small amount of methanol in the UHV, $(CH_3COCH_3)^-(CH_3OH)(H_2O)_{3,4}$ peaks are also present at this stage of the reaction. This suggests that a minimum of four solvents molecules, regardless of the type of solvent, is needed to stabilize the $CH_3COCH_3^-$ anion. $(CH_3COCH_3)^-(H_2O)_4$, as well as $(CH_3COCH_3)^-(CH_3OH)(H_2O)_3$, undergo a slow electron detachment.

Acetaldehyde behaves almost identical to acetone. The hydrated electron cluster efficiently take in only one acetaldehyde molecule and solvated $CH_3CHO^-(H_2O)_m$ anions are formed. After a single molecule of the reactant has entered the cluster, no further uptake of acetaldehyde is observed in the early stage of the reaction. Conversion of 50% of the initial distribution is reached fast, in less than 1 s. After 7 s the initial $(H_2O)_n^-$ clusters are again barely visible. The $CH_3CHO^-(H_2O)_m$ clusters then fragment, losing one by one the water molecules down to $CH_3CHO^-(H_2O)_3$. When the clusters are very small an endothermic ligand exchange takes place leading to the formation of $(CH_3CHO)_2^-(H_2O)_2$. We repeated the experiments using perdeuterated acetaldehyde, CD_3CDO. Similarly to the acetaldehyde, the $CD_3CDO^-(H_2O)_m$ clusters are formed, followed by fragmentation down to $CD_3CDO^-(H_2O)_3$. The intake of a second CD_3CDO molecule leads to $(CD_3CDO)_2^-(H_2O)_2$ formation. No H/D exchange is observed, even after long reaction delays. For both, acetaldehyde and perdeuterated acetaldehyde, after long reaction delays of 50 s, the signal has disappeared due to black-body radiation and collision-induced electron detachment [40].

Benzonitrile is one of the molecules which react with the electron inducing a ionic core exchange. The peaks corresponding to an uptake of one benzonitrile molecule $(C_6H_5CN)^-(H_2O)_m$ into the clusters are already visible at 0 s reaction delay. Once the free electron is not anymore available, the clusters start to exchange ligands. Thus, 2 s later the clusters have exchanged several water molecules for a second benzonitrile. From the offset of the cluster distributions one can approximate the number of water molecules exchanged for one benzonitrile to be 5 or 6. The clusters continue to fragment and exchange ligand molecules until, after 15 s reaction delay, five progressions of product peaks are visible, each containing 1–5 benzonitrile molecules. Clearly, the most intense peak distribution is $(C_6H_5CN)^-(H_2O)_n$, $n = 4–12$, with an intensity maximum at $m/z = 265$ and corresponding to $m = 9$ water molecules. After 20 s the clusters have completely exhanged or lost all the water molecules, and one can clearly identify $(C_6H_5CN)_m^-$, $m = 2–7$. At the same time two other distributions can be seen. The first one as intense as the products, with the peaks at $m/z = 266$, 369, 472, 575, 678 and the other about one-fifth with peaks at $m/z =$ 429, 532, 636. Both contain benzonitrile, but are shifted by 60 and 120 amu, respectively, to higher masses. We are not able to rationalize these products in terms of reaction with benzonitrile alone. The most probable explanation is that, at long reaction delays, due to the very high number of collisions, a minor, unidentified impurity in the benzonitrile solution, is taken in by the clusters. However, after additional 10 s, the impurity is lost from the clusters, and the products seen after 30 s are $(C_6H_5CN)_{2,3,4}{}^-$. After a total of 40 s reaction delay, the clusters have detached the electron and the signal is lost.

Another example for ionic core exchange are the reactions with NO reported in the literature by Johnson and coworkers [41,42]. These differ slightly from the O_2 and CO_2 reactions. Again, in the first reaction step, $NO^-(H_2O)_n$ is formed, where NO^- undoubtedly form the ionic core. $NO^-(H_2O)_n$, however, undergo at least to additional steps of ligand exchange, which is, however, conceptually different from the case (b). NO does not participate in the hydrogen bonded network, but rather forms strong bonds to NO^-. The $(NO)_3{}^-$ unit thus might be seen as the “real” ionic core of the cluster.

4.4. Rearrangement of covalent bonds (d)

One usually understands under chemical reaction a process, where chemical bonds between atoms are broken or formed, and strictly speaking, none of the processes discussed above really falls into this category. There are, however, numerous reactions where interaction with the hydrated electron does indeed result in a breakage of a real, covalent chemical bond, or formation of a new one, or both. Such reactions are very often initiated by a change in the nature of the ionic core of the $(H_2O)_n{}^-$ cluster. Very simple examples are the reactions with Br_2 and CH_3Br studied by Johnson and coworkers [42], which result in formation of $Br^-(H_2O)_n$. In these cases, the electron affinity of the Br atom of 3.36 eV is the driving force of the reaction, which in itself is sufficient for the bond cleavage in Br_2 and CH_3Br [42].

Repeating the experiments with N_2O under ICR conditions, we obtained results similar to the flow reactor study [41]. We also observe two different products, formation of $O^-(H_2O)_n$ and $OH^-(H_2O)_n$, with a branching ratio of approximately 3:1. Fig. 3 shows the temporal evolution of the mass spectra with reaction time. The branching ratio can best be seen in the mass spectra of the early stage of the reaction, which exhibit almost exactly three times the intensity for $O^-(H_2O)_{41}$, compared with $OH^-(H_2O)_{41}$. Initially, $O^-(H_2O)_n$ is formed by abstraction of the oxygen atom from N_2O, which will immediately recombine with the electron. In this initially hot cluster, isomerization of $O^-(H_2O)_n$ to $OH^-(OH)(H_2O)_{n-1}$ is energetically feasible, and an OH radical can be lost. $OH^-(OH)$ core switching competes with H_2O evaporation, and this competition would be responsible for the observed branching ratio.

Another, more complex example we have recently studied involves the reaction of hydrated electrons with acetonitrile [23]. Ab initio studies have shown that the nitrile carbon atom of CH_3CN may attach an additional hydrogen atom to form a relatively stable CH_3CHN radical [60]. The CH binding energy is, however, not sufficient to make a reaction such as, for instance, $CH_3CN + H_2O \rightarrow CH_3CHN + OH$, accessible. This situation, however, changes appreciably in the presence of an electron:

$$(H_2O)_n{}^- + CH_3CN \rightarrow OH^-(H_2O)_{n-m-1} + CH_3CHN + mH_2O \qquad (3)$$

The reaction (3) is assisted in the first place by the appreciable, 1.8277 eV electron affinity of the hydroxyl group.

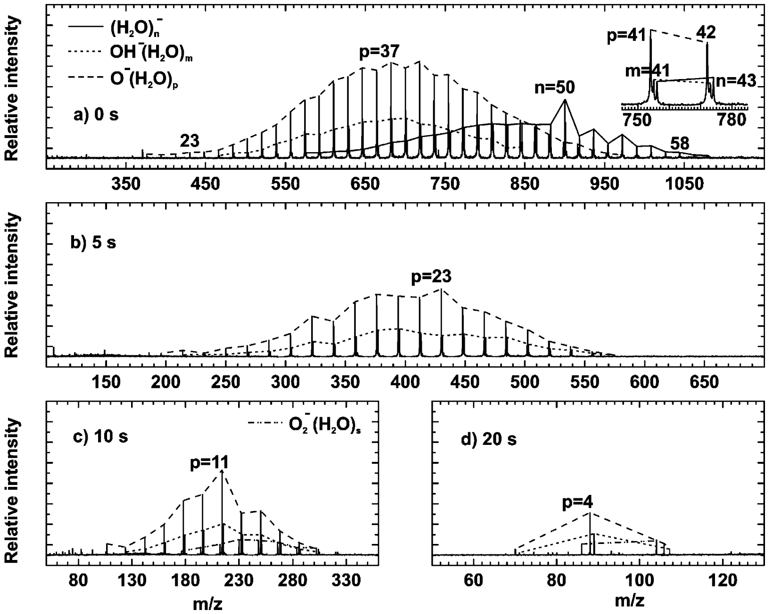

Fig. 3. Mass spectra of the reaction of $(H_2O)_n{}^-$ with N_2O after (a) 0 s, (b) 5 s, (c) 10 s and (d) 20 s. Already at 0 s two different product distributions are visible. Shifted lower by one amu are the $OH^-(H_2O)_m$, while a shift of 2 amu to the left corresponds to the $O^-(H_2O)_p$ products. After 5 s the initial hydrated electron clusters have completely reacted. The clusters fragment due to the black-body radiation to $OH^-(H_2O)_3$ and $O^-(H_2O)_3$. Species $O_2{}^-(H_2O)_s$ are present due to minor impurities of O_2, after long reaction delays.

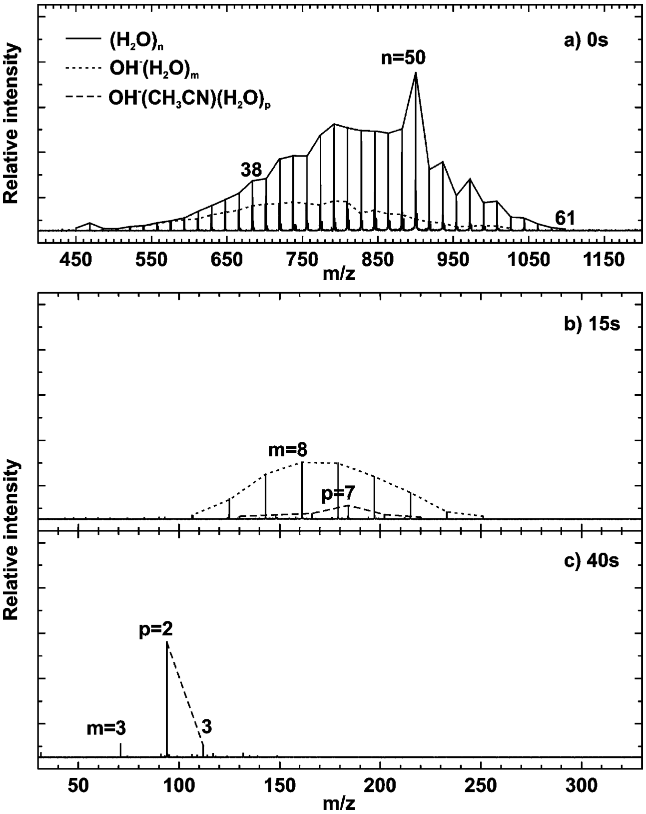

Fig. 4. Representative spectra illustrating the reaction of $(H_2O)_n{}^-$ with acetonitrile. At 0 s, shifted to lower masses by one amu, the products, $OH^-(H_2O)_m$, are visible. After 15 s the reaction products have fragmented to a cluster size where they are basic enough to allow the intake of one acetonitrile molecule. The clusters lose ligands until, after 30 s, the main products are $OH^-(H_2O)_3$, $OH^-(CH_3CN)(H_2O)_2$ and $OH^-(CH_3CN)(H_2O)_3$.

Furthermore, it is also promoted by the solvation energy of the relatively compact OH^- anion, which is considerably higher than that of the diffuse free electron. Accordingly, reaction (3) proceeds in the ICR cell spontaneously, and probably with close to the collision rate, as evidenced by the presence of a considerable concentration of the reaction product already at nominally $t = 0$ s in Fig. 4. In the presence of gaseous acetonitrile in the cell, the aqueous electron clusters lose a hydrogen atom, and are thus converted into hydrated hydroxyl anions. Using deuterated acetonitrile instead reveals that the methyl group is not involved in the reaction, and one of the aqueous protons is lost from the cluster. Like the reactions listed in the previous section, this reaction is also accompanied by a change in the ionic core of the cluster. Obviously, it again requires the presence of a free electron, and each cluster can therefore react only once. The product clusters containing the hydroxyl anion, $OH^-(H_2O)_n$, are, similar to clusters containing molecular oxygen, stable with respect to electron detachment due to the high electron affinity of the OH radical.

In our previous study we have shown that the hydrated hydroxyl anions, prepared directly in the ionic source, when left alone in the ICR cell gradually fragment, leaving $OH^-(H_2O)_3$ as a final product. This anion eventually reaches thermal equilibrium with the ambient temperature apparatus walls, and is effectively stable under our experimental conditions both with respect to electron detachment and with respect to further fragmentation. In the presence of gas phase acetonitrile in the cell, however, the small $OH^-(H_2O)_n$ clusters below about $n = 10$ can take up one additional CH_3CN molecule, undoubtedly due to its high basicity, as is evidenced in Fig. 4 after 15 s reaction delay. These then further fragment fragment losing either H_2O or CH_3CN molecules, yielding eventually the $OH^-(H_2O)_2(CH_3CN)$ cluster as a final product [39]. Interestingly, experiments with deuterium substituted acetonitrile reveal, that within this cluster a dynamical, proton transfer equilibrium is established:

$$(H_2O)_2(OH^-)(CH_3CN) \quad \leftrightarrow \quad (H_2O)_3(CH_2CN^-) \qquad (4)$$

When CD_3CN is used, repeated proton transfer processes according to Eq. (4) lead to a complete isotopic scrambling within the complex between the “organic” CH_3CN, and the aqueous, $OH^-(H_2O)_2$ parts. It is also interesting to note, that a single additional water molecule is sufficient to switch off this isotopic scrambling.

5. Conclusions

In the present manuscript we have reviewed studies of the reactions of hydrated electron clusters, $(H_2O)_n{}^-$, upon binary collisions with small molecules in the gas phase. The studies show, that the electrons undergo many reactions known from pulsed radiolysis experiments and similar studies, but also exhibit properties specific for finite clusters. Studies of such clusters trapped in an FT-ICR experiment have the advantages of less ambiguity, complete elimination of the effects of impurities, and in view of the long lifetime of the solvated electron the ability to study even very slow and inefficient reactions. In this way, the inherent chemical properties of the solvated electron can be probed.

We show that one can loosely classify the processes occurring upon binary collisions of the $(H_2O)_n{}^-$ clusters with small gas phase molecules into at least four distinct categories, collisional activation, ligand exchange, core exchange and rearrangement of covalent bonds. The representative examples for each of these categories reveal the rich and multifaceted reactions of free electrons, the simplest free radicals of them all.

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