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Transition states for hydride-water $(H^-)(H_2O)_n$ clusters, $n = 2$–6, 20

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ABSTRACT

Hydride anion (H^-) reacts quickly in aqueous solution to form molecular hydrogen (H_2) and hydroxide ion (OH^-), but $(H^-)(H_2O)_n$ clusters have many PES local minima in which the hydride is solvated by two or more water molecules making dihydrogen bonds. Using *ab initio* methods applied to $(H^-)(H_2O)_n$ clusters for $n \leqslant 6$ and for $n = 20$, we explored these clusters' reaction pathways and transition states. At the B3LYP/6–311++G** level of theory, all of the small $(2 \leqslant n \leqslant 6)$ clusters are unstable or barely stable at 0 K: all activation barriers for reaction to form H_2 are under 0.5 kcal/mol, all but one are under 0.2 kcal/mol, and most are negative. In some instances the lowest-barrier reaction pathway is multi-step, requiring H-bond rearrangements first, and those rearrangements are consistent with improving the "presolvation" of the emerging (OH^-) in accordance with a "solvation hierarchy." The arrangements explored for $n = 20$ consist of (H^-) encapsulated by a dodecahedral cage with coordination of 3, 4, 5, or 6 at the hydride anion. The lowest-energy $(H^-)(H_2O)_{20}$ cluster found has 4 H-bonds to the anion. Of several reaction pathways explored, the lowest barrier height is 3.68 kcal/mol at 0 K, suggesting that a low-temperature stable solvated hydride can exist. For the $(H^-)(H_2O)_{20}$ clusters at their transition states to H_2 formation, the H^-–H distances are at or below the van der Waals cutoff for covalent H—H bonding (92 pm). In all, 21 transition states to $(H_2)(OH^-)(H_2O)_{n-1}$ and eight H-bond rearranging transition states are presented. During a 25 ps AIMD simulation of H^- in a box of 32 H_2O's at 300 K, reaction to form H_2 did not occur, the hydride ion spent 95% of the time being 4-coordinated, and two first-shell exchanges were observed. This and other calculations suggest the mean survival time of (H^-) in bulk water at 300 K is likely between 20 and 100 ps.

1. Introduction

Understanding of hydride-water interactions is important for biological energy metabolism, fuel cell studies and nuclear materials research. In aqueous context, hydride transfer occurs during the formation of NADH from NAD^+ in the Krebs cycle [1], and Makoto [2] noted that solvation by a water cluster can lower the activation energy for H^- transfer in acycloin anions by 10 kcal/mol. Stable aqueous hydride anion has not been directly observed but there may be a steady-state population of short-lived solvated hydrides in some electrolysis systems [3,4]. Metal hydrides react quickly and irreversibly with water to produce dihydrogen gas and metal hydroxide. The interaction of solid LiH with bulk water to produce LiOH and H_2 has been extensively modeled as a two-step process [5–7]. The actual chemical reaction

$$(H^-)_{aq} + H_2O \rightarrow (H_2)_g + (OH^-)aq \tag{1}$$

is rapid, but it soon creates a surface-adjacent layer of dissolved LiOH that acts as a barrier, and then diffusion of water toward the surface and LiOH away from it become the rate-limiting first step.

The project described here used *ab initio* methods to study the reaction (1) in small and medium size water clusters. Lee et al. [8] demonstrated that $(H^-)(H_2O)_n$ clusters can have multiple PES local minima for $n \leqslant 6$, but for $n > 1$ they did not look at transition states. We were particularly interested in assessing the transition energy barriers for (1) in clusters and exploring whether any structural attributes of $(H^-)(H_2O)_n$ clusters might render them longer-lived. Interestingly, for $n = 1$, i.e. reaction (1) in gas phase, the reaction is endothermic [9]. The global minimum geometry for $(H_3O)^-$ has H^- solvated by one H_2O, but for $n \geqslant 2$, where the hydroxide ion can be solvated by one or more H_2O's, (1) becomes exothermic and the global minimum has the form $(H_2)(OH^-)(H_2O)_{n-1}$. At PES local minima for $n \geqslant 2$, $(H^-)(H_2O)_n$ clusters have the anion solvated by two or more H_2O units forming dihydrogen bonds [10]. Characteristics of the H–H interaction in dihydrogen bonds, including its length range and correlation of length with O–H stretch frequency, are similar to those of other O–H - - X hydrogen bonds [11–13].

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Kelly and Rosseinsky [4] used a variety of methods to predict properties of the short-lived solvated H^- species. They particularly noted the similarity of solvated H^- to solvated F^-. Bringing several experimental methods to bear on the question, their estimates for the ratio of H^- radius to F^- radius, $\rho(H^-/F^-)$, ranged from 1.03 to 1.09. The pKa of H_2 in H_2O was estimated to be 22 ± 2 at 25 °C. Gibbs free energy of formation of H^- in aqueous solution $\Delta_f G^0$ was found to be 141 ± 4 kJ/mol at 25 °C, while free energy of solvation (from gas phase at STP into H_2O) was found to be −421 ± 4 kJ/mol at 25 °C.

The similarity of H^- to F^- means that, like fluoride, the hydride anion would be expected to occupy the interior of a medium-size solvating cluster, whereas Cl^-, Br^-, and I^- prefer to remain at the surface [14–18]. This prediction was supported by our calculations and one question we were interested in was the optimum coordination number for solvated H^-. Heuft and Meijer [19] conducted a molecular dynamics simulation for solvated F^- and found the average coordination number to be 5 and the average dwell time of each solvating H_2O to be 16 ps. During their 20 ps simulation several H-bonds to fluoride formed and broke, maintaining the coordination of F^- between 4 and 6. Our 25 ps AIMD simulation of solvated hydride was done in part to look for similarities and differences between solvated hydride and fluoride.

We had four goals for the project. We wondered about the stability of small and medium-sized $(H^-)(H_2O)_n$ clusters, which we addressed by computing transition states. Second, we wanted to know how aspects of the cluster's topology (or H-bond connectivity pattern) could be enhance or impede reactivity, and whether any unifying principle(s) could explain the variety of reaction pathways. Third, we wondered low long the longest-lived hydrated hydride clusters might last. Lastly, through AIMD we explored how the finite cluster findings might translate to bulk liquid.

To approximate H^- in the context of bulk water we placed H^- inside a 5^{12} dodecahedral H_2O cage. Dodecahedral $(H_2O)_{20}$ has been much studied [20–23] because of its occurrence as a magic number [24–26] and its importance as a building block of von Stackelberg's Type I clathrate hydrate [27,28]. There is no experimental evidence for or against a dodecahedral geometry for $(H^-)(H_2O)_{20,}$ but it is a plausible setup for a finite model of "hydride surrounded by water." The huge number of possible isomers meant we had to fix some parameters in order to obtain meaningful comparisons. In the dodecahedral $(H^-)(H_2O)_{20}$ several free H's point inward toward the anion. We postulated this could raise the cluster's transition energy barrier because as soon as the (H^-) approaches any one of the solvating donor H's and begins to react with it to form H_2, the result is suddenly a cage with several free H's pointing inward toward a neutral molecule, which is an energetically unfavorable arrangement. This prediction was borne out and probably represents our single biggest insight into the possible longevity of solvated hydride in bulk water.

2. Methods

Static *ab initio* calculations were done on a Parallel Quantum Solutions (PQS) QuantumCube, using PQS parallel software [29]. Relaxed PES scans for ground state electronic energy, denoted E^0, as a function of H^-– H distance, denoted d_{HH}, were the principal device for locating transition states. All reported transition states (also called "*t*-states") were first verified by a Hessian calculation. The *t*-state was then nudged slightly by adding or subtracting a small multiple of the "negative" eigenvector and gradient-following optimization was restarted using a small step size of 0.1 or less, to verify which local minima are reached going in both directions toward local minima. This is not identical with an intrinsic reaction coordinate (IRC) calculation [30–32], which would be the ideal method for determining a reaction pathway but is considerably more computation-intensive. For all but one of our pathways leading toward an $(H^-)(H_2O)_n$ geometry, there is no ambiguity about which isomer is the endpoint (the exception is discussed when we get to it). For pathways leading to $(H_2)(OH^-)(H_2O)_{n-1}$ geometries from *t*-states, a series of "choices" between competing rearrangements may need to be made about which way to proceed downhill, and the optimization method might sometimes make choices different from the IRC method. Therefore we do not claim that the $(H_2)(OH^-)(H_2O)_{n-1}$ isomers reported are always the exact isomers that would occur experimentally. Comparing and distinguishing among $(H_2)(OH^-)(H_2O)_{n-1}$ isomers might be an interesting subject but was not a focus of this project.

For all but the smallest clusters, B3LYP/6−311++G** was the method of choice to balance accuracy with computational tractability. In addition to its well-established use in water cluster studies in general, Swart [33] demonstrated the validity of DFT for H^+ affinity of solvated anions, and B3LYP/6−311++G** underwent further benchmarking against high-level MP2 for $(H^-)(H_2O)_n$ clusters by Lee et al. [8]. While DFT with a large basis is certainly a usable model for these systems, it does underestimate slightly the strength of a dihydrogen bond compared to MP2. Throughout this article, "B3LYP" will mean B3LYP/6−311++G** and "MP2" will mean MP2/aug-cc-pVTZ unless otherwise indicated. All reaction pathways we describe or show were computed with B3LYP except where they are specifically indicated to be MP2.

Ab initio molecular dynamics (AIMD) simulation applied the Vienna atomistic simulation package [34] (VASP) version 4.6, the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional [35], and projected-augmented wave (PAW) pseudopotentials [36,37]. The default energy cutoffs for H and O were 400 eV. The cubic simulation cell contained one H^- anion and 32 H_2O molecules, and had edge length 9.8552 A, corresponding to a water density of 1.0 g/cc. A neutralizing charge background was added. A time step of 0.25 fs and an energy cutoff of 400 eV were adopted, and a Born–Oppenheimer convergence of 10^{-6} eV was enforced at each time step. These parameters limit the temperature drift to about 1 K/ps. A Nose thermostat was applied to maintain the temperature at $T = 300$ K. The deuterium mass was substituted for all protons to allow a larger time step, although the H mass is assumed whenever water density is reported. We continued the trajectory for 10^5 steps, representing 25 ps.

The initial AIMD configuration was prepared as follows. We started with the core $H^-(H_2O)_4$ of an optimized cluster, Dod-4A, to be described later. This core was held frozen while additional water molecules were added to yield a 1.0 g/cc density. These mobile water molecules were allowed to equilibrate at $T = 300$ K for 40 ps using classical force field-based molecular dynamics simulations. The final configuration thus generated was equilibrated using AIMD at $T = 300$ K for 2 ps before starting the collection of statistics for the next 25 ps.

3. Results: $2 \leqslant n \leqslant 6$

Table 1 summarizes all stationary states for $(H^-)(H_2O)_n$ clusters, $2 \leqslant n \leqslant 6$, that are mentioned in this article, along with their relative electronic energy (E^0) and relative free energy values (free energy at 0 K is computed as $G^0 = E^0 + \text{ZPE}$), dipole moments, and d_{HH} distances for the "index" or reacting proton.

3.1. n = 2

The single PES minimum geometry for $(H^-)(H_2O)_2$ was first described by Melin and Ortiz [38] as "Complex A". It has both waters solvating the hydride ion and one H-bond between the waters. The