

The Aqueous Proton Is Hydrated by More Than One Water Molecule: Is the Hydronium Ion a Useful Conceit?

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ABSTRACT: For some time now, there has been disagreement concerning the best way to denote the aqueous proton in chemical equations. Recent results have shown that although the hydronium ion, H_3O^+ , may exist as a participant in some kinetic mechanisms, the thermodynamic ground-state structure for the hydrated proton is actually the hexahydrate, $\text{H}^+(\text{H}_2\text{O})_6$, or $\text{H}_{13}\text{O}_6^+$. We report here a short history of this debate and a brief summary of the recent spectroscopic results. Finally, we argue that in the overwhelming majority of reactions studied in lower-division college and high school chemistry courses, it is preferable to use $\text{H}^+(\text{aq})$ rather than $\text{H}_3\text{O}^+(\text{aq})$ to depict the hydrated proton.

KEYWORDS: First-Year Undergraduate/General, High School/Introductory Chemistry, Upper-Division Undergraduate, Inorganic Chemistry, Physical Chemistry, Misconceptions/Discrepant Events, Acids/Bases, Aqueous Solution Chemistry, Hydrogen Bonding

Recently in this *Journal* there was disagreement concerning the best way to denote the aqueous proton in chemical equations, with Ault¹ supporting the hydronium ion form often seen in textbooks, $\text{H}_3\text{O}^+(\text{aq})$, and Moore et al.² favoring the older, simpler signifier, $\text{H}^+(\text{aq})$. One of the main reasons why Ault and others support the use of the hydronium ion is that when an acid ionizes in water, it is convenient to identify a single water molecule as the proton-accepting base, yielding the hydronium ion conjugate acid. But Moore et al., summarizing results from Saykally and Blake³ and Castleman et al.,⁴ wrote that when an acid ionizes, the base is actually a cluster of 10 or more⁵ water molecules.² Further support for the recommendation by Moore et al. to use $\text{H}^+(\text{aq})$ instead of $\text{H}_3\text{O}^+(\text{aq})$ includes the argument that, unless it is especially relevant, we do not specify the number of water molecules in the hydration shell of other ions (e.g., we write $\text{Co}^{2+}(\text{aq})$, not $\text{Co}(\text{OH}_2)_6^{2+}$), “so why should H^+ be treated differently?”⁶

Since the publication in 2010 of the Moore and Ault articles, substantial progress has been made in the spectroscopic characterization of the structure of the hydrated proton ($\text{H}^+(\text{H}_2\text{O})_n$) in liquid water. In this commentary, I will briefly review the recent results, which serve to bolster the argument against the pedagogic use of the hydronium ion.

■ STRUCTURE OF THE HYDRATED PROTON

We begin with the simple question: How many waters are actually in the hydration shell of the proton; in other words, what is the value of n ? Before 1980 the favored values were (a) $n = 1$, the hydronium ion, sometimes called the Eigen ion⁷ (Figure 1, compound 1); (b) $n = 2$, often called the Zundel ion⁸ (Figure 1, compound 3); and (c) $n = 4$: Eigen cited evidence for this tetrahydrate as the hydrated complex of the hydronium ion,⁷ that is, $\text{H}_3\text{O}^+(\text{OH}_2)_3$ (Figure 1, compound 2).

The Hydronium Ion

In 2006, Stoyanov et al.¹² showed that the H_3O^+ ion ($n = 1$) exists only in a very limited set of circumstances. In wet organic

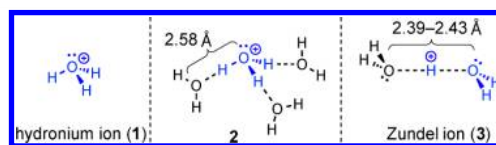


Figure 1. Pre-1980 putative structures of the hydrated proton. (1) $n = 1$, the hydronium ion; (2) $n = 4$, the trihydrated hydronium ion, with $\text{O}\cdots\text{O}$ distance = 2.58 Å⁹; (3) $n = 2$, the Zundel ion, with $\text{O}\cdots\text{O}$ distance = 2.39–2.43 Å.^{10,11}

solvents, it is *always* (emphasis C. A. Reed¹³) trisolvated, for example, $\text{H}_3\text{O}^+(\text{C}_6\text{H}_6)_3$. In aqueous solution, Reed has argued¹³ that the hydronium and/or Zundel ions (3) may exist briefly as kinetically important intermediates in reaction mechanisms,¹⁴ but not as thermodynamically stable entities. It turns out that the IR criteria used for decades to support the existence of the hydronium ion as a thermodynamically stable molecule were incorrect.^{12,13,15,16}

The Zundel Ion

Good evidence for the existence of the Zundel ion ($n = 2$), and also H_7O_3^+ ($n = 3$), is limited (so far) to organic solvents.^{11–13} For example, the Zundel ion is the predominant cation for a number of strong acids in wet acetonitrile.¹⁷ On the other hand, “this ion is always tetrasolvated with traditional H-bonds from the four terminal OH groups... $\text{H}_5\text{O}_2^+(\text{solvent})_4$.”¹³ When some acids ionize in wet organic solvents, the core ion structure is H_7O_3^+ solvated by up to five solvent molecules (or anions).^{13,18} This form, in which H^+ is delocalized over *three* water molecules, has its own unique IR spectrum.¹⁸

The Hexahydrate

But what about H^+ in aqueous solution? It turns out that in 2010, while the H^+ versus H_3O^+ discussion was going on in the pages of this *Journal*, Stoyanov et al. reported their results from “exacting IR difference spectroscopy”.¹³ Their conclusion: $n = 6$.^{15,16} Moreover, the IR spectrum of $\text{H}^+(\text{aq})$ was interpreted in

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terms of a symmetrical $\text{H}_{13}\text{O}_6^+$ ion: This ion differs slightly from the tetrahydrated Zundel ion, $(\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2)\cdot(\text{H}_2\text{O})_4$, in having a greater delocalization of positive charge, and a longer central $\text{O}\cdots\text{O}$ distance (see Figure 2).

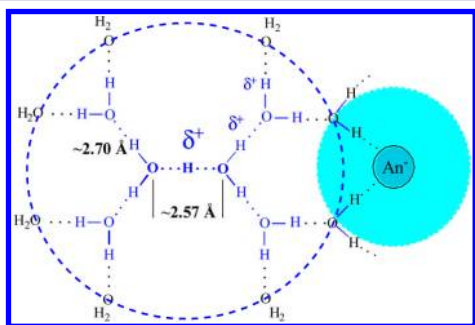
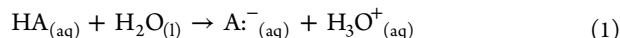


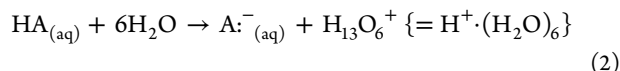
Figure 2. Structure of the $\text{H}_{13}\text{O}_6^+$ ion in water, including an unusually long central $\text{O}\cdots\text{H}^+\cdots\text{O}$ distance: 2.57 Å as opposed to the expected 2.39–2.43 Å for typical Zundel ion tetrasolvates. The blue dashed circle indicates the extent of positive charge delocalization. The circled turquoise An^- represents the ion-paired counterion. Reprinted from ref 16 with permission of The Royal Society of Chemistry. Copyright 2011, The Royal Society of Chemistry.

ACID IONIZATION EQUATIONS

Most textbooks treat acid (HA) ionization in water as a reaction in which a single water molecule serves as the proton-accepting (Brønsted–Lowry) or lone-pair-donating (Lewis) base, as depicted in eq 1:



For example, Brown and LeMay et al.¹⁹ state that “the interaction of a proton with water forms the hydronium ion, H_3O^+ ... We often use the notation H^+ for simplicity and convenience.... The notation H_3O^+ , however, more closely represents reality.” This is inconsistent with the results of Stoyanov et al.,^{13,15,16} who conclude that protonated water is a hexahydrated cluster that lacks any H_3O^+ hydronium ion character. Accordingly, one could make an argument that the actual Brønsted or Lewis base in the acid ionization reaction is actually a hexahydrate cluster, as specified in eq2:



Although thermodynamically accurate, eq 2 is unnecessarily cumbersome. Instead, we recommend the simplest equation, depicted in eq 3:



In the reactant $\text{HA}_{(\text{aq})}$ in this equation, the “aq” represents the waters of hydration, which serve to increase the polarization of the H–A polar covalent bond until it cleaves heterolytically. In the product $\text{H}^+_{(\text{aq})}$, the “aq” is now understood to represent the hexahydrated proton depicted in Figure 2 and supported by the spectroscopic results from Stoyanov et al. summarized above. Equation 3 has the double advantage of being simpler than the $\text{H}_{13}\text{O}_6^+$ in eq 2, and truer than the H_3O^+ in eq 1, often seen in textbooks. The implication of eq 3 is that acid ionization is not a simple Brønsted–Lowry/Lewis type of reaction: The proton is *not* transferred to a single-molecule base that forms a stronger bond than the H–A bond (as implied in eq 1).²⁰ Instead, acid

ionization must be viewed as a reaction in which the H–A bond is weakened by the entire surrounding hydration shell. One might add that these considerations apply only to acid ionization and the hydrated proton; true acid–base reactions involving proton transfer between single-molecule acids and bases are still accurately described by Brønsted–Lowry (or Lewis) formalism.

UPPER-DIVISION EXPLORATIONS

Advanced-level instructors and students who wish to explore some of the more subtle aspects of the aqueous proton are referred to the fine new review by Chris Reed.¹³ The most intriguing findings include (a) the dicoordination that prevails when acids ionize in dry organic solvents, forming $\text{H}(\text{solv})_2^+$; (b) the prevalence of the trihydrated H^+ in the H_7O_3^+ ion when acids ionize in wet organic solvents; and (c) the indication from a continuous broad absorption across the IR spectrum of $\text{H}^+_{(\text{aq})}$ that in $\approx 70\%$ of the $\text{H}^+\cdot(\text{H}_2\text{O})_6$ clusters, proton movement within the Zundel-like $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ core is faster than the IR time scale. The consequence of this is that in reaction kinetics, only one or two of the waters of hydration will appear in the rate law. So whereas the hydronium (H_3O^+) and Zundel (H_5O_2^+) ions may appear to be kinetically significant in certain reactions, the proton hexahydrate $\text{H}^+\cdot(\text{H}_2\text{O})_6$ is the most thermodynamically accurate description of $\text{H}^+_{(\text{aq})}$.

REMOVING THE HYDRONIUM ION FROM TEXTBOOKS

It has been argued that with respect to the hydrated proton, the hydronium ion is a useful conceit because it (a) “closely represents reality”;¹⁹ (b) is the “simplest form”;²¹ and (c) “often prompt[s] instructors to explain a more realistic picture.”²² If (c) were *always* true, then H_3O^+ would be a useful depiction and there would be no need for this commentary. However, the quote from a popular introductory chemistry textbook, in (a) above, shows that some authors and instructors (and of course, students!) believe erroneously in the reality of the hydronium ion. Depicting the hydrated H^+ cation as $\text{H}^+_{(\text{aq})}$ is both simpler and less misleading than using $\text{H}_3\text{O}^+_{(\text{aq})}$.

Finally, to understand the nature of $\text{H}^+\cdot(\text{H}_2\text{O})_6$, would not students “need to understand the solvation process and aspects of coordination chemistry (Lewis acid–base adducts)?”²¹ Quite so, and this makes the aqueous proton a fitting topic for discussion in inorganic chemistry courses (see discussion above in the Upper-Division Explorations section). The beauty of the $\text{H}^+_{(\text{aq})}$ designation is that it communicates a simple but still accurate depiction of the hydrated proton without requiring a detailed knowledge of coordination chemistry. $\text{H}^+_{(\text{aq})}$ is thus the most suitable signifier of the aqueous proton in reactions studied in lower-division chemistry courses.

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Notes

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this *Journal* on recent discoveries concerning this very important ion, the solvated proton.

(22) Editor, personal communication, 2013.

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