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Myths about the Proton. The Nature of H^+ in Condensed Media

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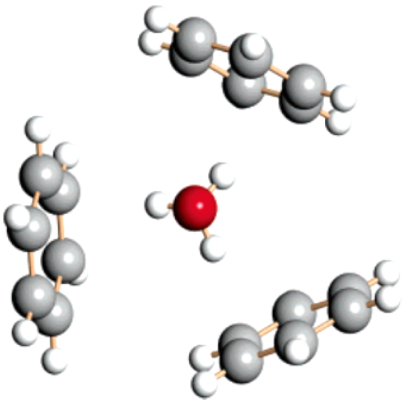

Recent research has taught us that most protonated species are decidedly not well represented by a simple proton addition. What is the actual nature of the hydrogen ion (the "proton") when H^+, HA, H_2A^+, and so forth are written in formulas, chemical equations, and acid catalyzed reactions? In condensed media, H^+ *must* be solvated and is nearly always dicoordinate, as illustrated by isolable bisdiethyletherate salts having $H(OEt_2)_2^+$ cations and weakly coordinating anions. Even carbocations such as protonated alkenes have significant C—H···anion hydrogen bonding that gives the active protons two-coordinate character.

Hydrogen bonding is everywhere, particularly when acids are involved. In contrast to the normal, asymmetric O—H···O hydrogen bonding found in water, ice, and proteins, short, strong, low-barrier (SSLB) H-bonding commonly appears when strong acids are present. Unusually low frequency IR νOHO bands are a good indicator of SSLB H-bonds, and curiously, bands associated with group vibrations near H^+ in low-barrier H-bonding often disappear from the IR spectrum.

Writing H_3O^+ (the Eigen ion), as often appears in textbooks, might seem more realistic than H^+ for an ionized acid in water. However, this, too, is an unrealistic description of $H_{(aq)}^+$. The dihydrated H^+ in the $H_5O_2^+$ cation (the Zundel ion) gets somewhat closer but still fails to rationalize all the experimental and computational data on $H_{(aq)}^+$. Researchers do not understand the broad swath of IR absorption from $H_{(aq)}^+$, known as the "continuous broad absorption" (*cba*). Theory has not reproduced the *cba*, but it appears to be the signature of delocalized protons whose motion is faster than the IR time scale. What does this mean for reaction mechanisms involving $H_{(aq)}^+$?

For the past decade, the carborane acid $H(CHB_{11}Cl_{11})$ has been the strongest known Brønsted acid. (It is now surpassed by the fluorinated analogue $H(CHB_{11}F_{11})$.) Carborane acids are strong enough to protonate alkanes at room temperature, giving H_2 and carbocations. They protonate chloroalkanes to give dialkylchloronium ions, which decay to carbocations. By partially protonating an oxonium cation, they get as close to the fabled H_4O^{2+} ion as can be achieved outside of a computer.

1. Introduction

Writing H^+ for the proton covers a multitude of sins. The problem begins with nomenclature. We are wedded to calling H^+ a proton when we really mean a hydrogen ion or Hydron.[1] A proton is an electron-free elementary particle of physics *or* the ^1H isotope. It would be quixotic to try and change our habits in this regard. The use of "the proton" is far too useful. But to put this into perspective, an electron-free proton has an estimated acidity 10^{56}(!) times greater than 100% H_2SO_4, the threshold of superacidity.[2] Adding a bare proton to a molecule is a real event in the gas phase, but only a *solvated* hydrogen ion can be transferred in condensed phases.

Semantics aside, what is the real identity of a protonated species in condensed media? The size and mobility of the actual proton carrier is important throughout biology, particularly where proton pumping[3] and accessibility to a reaction center is important.[4] The prevalence of water molecules over amino acid residues as H^+ carriers has been noted,[5] giving importance to the structure and proton mobility of $H(H_2O)_n^+$ species in proteins and proteinlike environments (i.e., organic solvents). The degree of water solvation of H^+ markedly affects the rates of protonation chemistry,[6] particularly in proton relay (shuttle) mechanisms[7−9] and coupled proton/electron transfer.[10]

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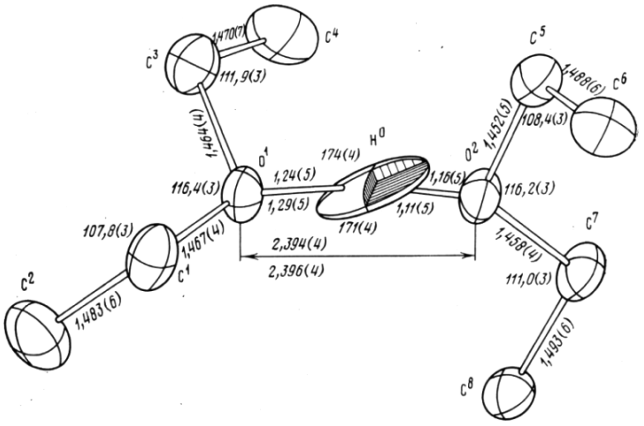


FIGURE 1. Historic early X-ray structure of the $H(OEt_2)_2^+$ cation that showed two-coordination of H^+ and captured the essence of the delocalized or averaged location of H^+ involved in short, strong, low-barrier (SSLB) H-bonding. Reproduced from ref 12 with kind permission from Springer Science+Business Media B.V.

Most protonation reactions are misrepresented by a simple proton addition. A self-ionizing acid HA is very unlikely to form a monoprotonated H_2A^+ cation, as is commonly written (eq 1)

$$2HA = H_2A^+ + A^- \quad (1)$$

More likely is a two-coordinate core cation, [HA···H^+···AH], with positive charge delocalization extended through additional H-bonded HA molecules.[11] It is better represented by eq 2.

$$3HA = [HA\cdots H^+\cdots AH] + A^- \quad (2)$$

Correctly and widely recognized is the *di*-solvated salt of the $H(OEt_2)_2^+$ cation formed when strong acids dissolve in diethyl ether (Figure 1).[12] Indeed, a major lesson learned from the past decade of research on H^+ in condensed phases is that the hydrogen ion is almost invariably *two*-coordinate. Even the seemingly *mono*-coordinate H^+ of the benzenium ion, derived from protonating benzene, has substantial C–H···anion hydrogen bonding at the protonated carbon atom (Figure 2).[13] Similarly, *t*-butyl cation (i.e., protonated *iso*-butene) salts are significantly stabilized by C–H···anion H-bonding[13] (possibly trumping hyperconjugation[14]), again illustrating the propensity of acidic H atoms to become two-coordinate (or higher, when bifurcated CH hydrogen bonding is involved). See Figure 3.[14]

Writing H_3O^+ (the Eigen ion)[15] might seem more realistic than H^+ for an ionized acid in water, but this too is a highly inaccurate description of $H_{(aq)}^+$ that still appears regularly in textbooks. The two-coordinate hydrogen ion in the $H_5O_2^+$ cation (the Zundel ion)[16] gets closer but still fails to fully rationalize the IR spectrum of $H_{(aq)}^+$.[17,18] In contrast to the typical asymmetric H-bond found in proteins (N–H···O) or ice (O–H···O), the short, strong, low-barrier (SSLB) H-bonds found in proton disolvates, such as $H(OEt_2)_2^+$ and $H_5O_2^+$, deserve much wider recognition.

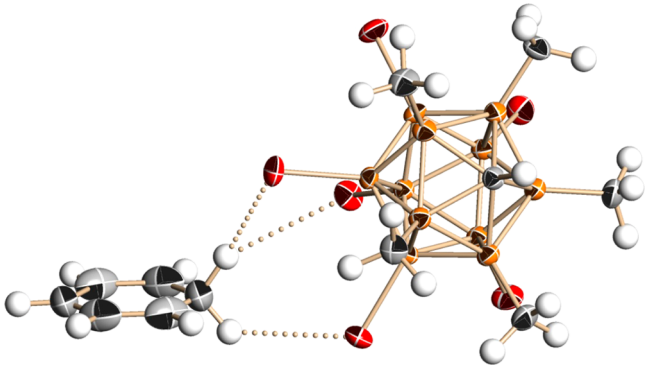


FIGURE 2. X-ray structure of the benzenium ion salt $[C_6H_7^+][CHB_{11}Me_5Br_6^-]$[33] showing CH···Br hydrogen bonding of the acidic CH_2 group at the protonated C atom.

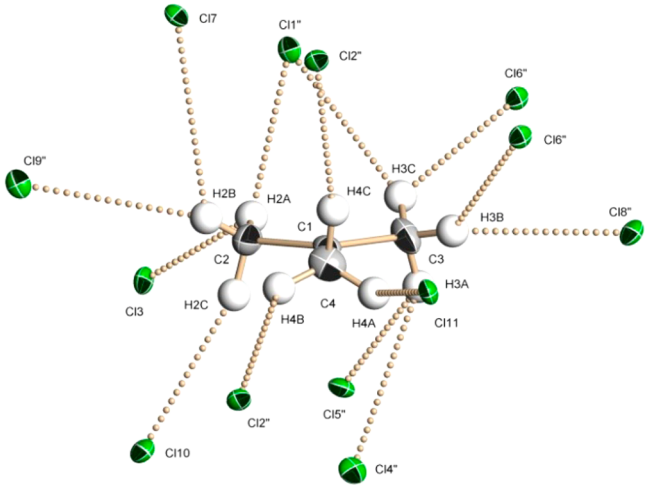


FIGURE 3. X-ray structure of the *t*-butyl cation salt $[C_4H_9^+][CHB_{11}Cl_{11}^-]$ showing CH···Cl hydrogen bonding, some of which is *bi*-furcated (e.g., to H3A, H3B and H3C). Reproduced from ref 14 by permission of The Royal Society of Chemistry.

The tendency to think of protonation in terms of a simple H^+ addition is not just due to the ease of writing it that way. For the past four decades, experimental studies on protonation have been largely confined to the gas phase where, because of low pressure, the shared-proton H^+ species found in condensed phases are rarely encountered. Moreover, the accompanying emphasis on theoretical descriptions of protonation frequently involved computations that omitted anions and treated solvents in an abstract manner. Earlier still, in the pioneering experimental work of Gillespie[19] and Olah et al.[20] in liquid superacids, protonation targets

were typically at low concentration compared to acid. So *mono*-protonation was also the expected result. However, such superacidic media are rarely used in everyday acid/base chemistry and, in the important areas of acid catalysis and biological acidity, low concentrations of H^+ are the rule. And with that comes proton *di*-solvation.

This Account highlights recent insights into the nature of H^+ in condensed media from our laboratories. Particular interests have been (a) making the strongest acid, (b) approaching the *di*cationic H_4O^{2+} ion, (c) the prevalence of *di*-solvation of H^+, (d) IR criteria for short, strong, low barrier (SSLB) H-bonding, (e) the nature of $H(H_2O)_n^+$ cations in wet (i.e., typical) organic solvents, and (f) the unique nature of H^+ in water, one of the oldest unsolved problems in chemistry.

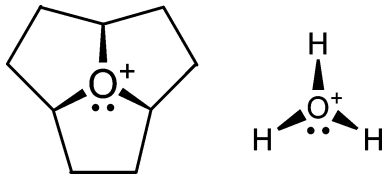
2. The Strongest H^+ Acid

For the past decade, the strongest pure acid has been the carborane acid $H(CHB_{11}Cl_{11})$[21,22] or possibly the comparable isoelectronic, diprotic $H_2(B_{12}Cl_{12})$.[23] This has been established in all phases: in *solution* using the Fărcașiu and Ghenciu[24] mesityl oxide $\Delta\delta^{13}$C NMR method in liquid SO_2 and by the fact that these acids protonate benzene, in the *solid state* as trioctylammonium salts using the νNH IR anion basicity scale,[25] and in the *gas phase* by calculating[26] and measuring[27] record-low deprotonation enthalpies. High solution acidity can of course be obtained with traditional mixed Brønsted/Lewis acids, for example, Magic Acid ($HFSO_3/SbF_5$), but the presence of redox-active Lewis acids such as SbF_5 introduces significant disadvantages: corrosiveness and basicity suppression.[28]

Carborane acids are said to be "strong yet gentle" because, despite their great acid strength, they do not engage in the corrosive redox chemistry of traditional mixed superacids. This is because of the extraordinary inertness of carborane anions[29] compared to the oxyanions and haloantimonates of traditional superacids. As a consequence, protonation chemistry via carborane acids is frequently cleaner than with traditional superacids, and this has led to the easier isolation of fragile species such as protonated C_{60},[30] phosphabenzenes, phosphazenes, and so forth and imparted remarkable stability to classic cationic intermediates of organic chemistry: *t*-butyl$^+$ (Figure 3), the $C_6H_7^+$ benzenium ion (Figure 2), and so forth.[28]

With the potential exception of acids based on perfluoroalkylsulfonamide analogues of triflic acid[31] or by using cooperative strategies,[32] the prospects for synthesizing a class of acids stronger than carborane acids appear slim. Quite simply, there does not appear to be any other class of anion that fits the dual requirements of lower basicity than a carborane anion and, critically, chemical stability toward H^+. Anions such as perfluorinated tetraarylborates are weaker bases than carboranes,[25] but they decompose when attempts are made to prepare their conjugate acids.[33]

SCHEME 1. Analogy of an Oxatriquinane Oxonium Cation (left) to the H_3O^+ Ion (right)



Per*fluor*inated CB_{11} carborane or B_{12} boron cluster anions[34] are less basic than their per*chlor*inated counterparts,[25,26] so their conjugate acids are expected to be stronger than $H(CHB_{11}Cl_{11})$. The preparation of fluorinated carborane acids has been achieved[35] and a demonstration of the superior acidity of $H(CHB_{11}F_{11})$ is seen in the protonation of alkanes. Remarkably, $H(CHB_{11}F_{11})$ protonates butane to form *t*-butyl cation *at room temperature* whereas $H(CHB_{11}Cl_{11})$ requires elevated temperatures to complete the same reaction (eq 3).

$$C_4H_{10} + H(CHB_{11}F_{11}) \rightarrow [t\text{-}Bu^+][CHB_{11}F_{11}] + H_2 \quad (3)$$

Thus, $H(CHB_{11}F_{11})$ is now the strongest pure acid known. Unfortunately, it is a lot of work to synthesize even small amounts and its ultrahigh acidity is easily lost via hydration by adventitious water when $[H(H_2O)_n^+][CHB_{11}F_{11}^-]$ salts are formed.

One recent intriguing application of the strength of $H(CHB_{11}Cl_{11})$ is the demonstration by IR of H-bonding to the lone pair of an oxatriquinane cation.[36] Oxatriquinanes are tricyclic analogues of the H_3O^+ ion (Scheme 1). H-bonding to the remaining lone pair of the O atom octet (Figure 4) is as close as one can get, outside of a computer, to the formation of a tetravalent oxygen species with a formal 2+ charge, that is, an analogue of the H_4O^{2+} ion.

Another illustration of the acid strength of $H(CHB_{11}Cl_{11})$ is the ready protonation of chlorocarbons. For example, chloroethane is protonated with loss of HCl (eq 4) to give isolable diethyl chloronium ion salts[37] which decay to previously unrecognized oligomeric carbocations.[38]

$$2EtCl + H(CHB_{11}Cl_{11}) \rightarrow [EtClH^+][CHB_{11}Cl_{11}^-] + EtCl \rightarrow [Et_2Cl^+][CHB_{11}Cl_{11}^-] + HCl \quad (4)$$

The linear polymeric structure of $H(CHB_{11}Cl_{11})$[39] nicely illustrates the propensity of strongly acidic protons to be

two-coordinate (Figure 5). Although the bridging acidic protons cannot be located with certainty in the X-ray structure, the IR spectrum is notable for the lack of bands in the range 2000−2500 cm^{-1}, the normal region for νHCl bands. Only broad bands at low frequency are visible, indicating that H^+ is located more symmetrically between Cl atoms on carborane anions. The IR is indicative of short, strong, low-barrier (SSLB) H-bonding[40,41] which has been studied more fully in proton disolvates with O-atom donors, described in the following section.

3. Two-Coordination and SSLB Hydrogen Bonding

There is a high level of awareness of proton *di*-solvation in salts of the $H(OEt_2)_2^+$ cation because of the wide utility of this oxonium salt in organometallic chemistry.[42,43] More recently, the generality of HL_2^+ proton disolvates has been established with a variety of O-atom and N-atom donor solvents (L = ethers, ketones, amines, etc.) using weakly coordinating counterions (carboranes, oxyanions such as ClO_4^-; complex haloanions such as SbX_6^-).[44] Acetonitrile is a more complicated solvent giving rise to many byproducts from protonation.[45] More coordinating anions such as Cl^- can of course replace a solvent molecule but *two*-coordinated H^+ is usual.

When subjected to X-ray crystal analysis, most proton disolvates of O-atom solvents show characteristically short O···O separations in the range 2.37−2.43 Å.[44] These can be compared to the longer average distance of ca. 2.56 Å found in ice or in protonated water clusters where normal, unsymmetrical O−H···O hydrogen bonding is present.[46,47] Short O···O distances are an indicator of *low-barrier* H-bonding.[40,41] The proton potential energy diagrams for these two types of H-bonding are illustrated qualitatively in Figure 6. The barrier for H^+ motion within an interval between the O atoms (see box around H in Figure 6, right) is so low that the location of H^+ becomes indeterminate, with unusual consequences for the IR spectrum. Conceptually, a completely *flat*-bottomed potential may exist but evidence is found only in certain neutron diffraction studies of carboxylate dimers.[48] The use of the word "strong" in "short, strong, low-barrier" (SSLB) does not imply that the low barrier imparts any particular additional bond strength to the H-bond.[48] It simply means that low-barrier H-bonds occur in the general realm of relatively strong H-bonding.

A convenient indicator of short, strong, low-barrier (SSLB) H-bonding is the very low frequency of νOHO. Instead of νOH in the familiar range near 3000 cm^{-1}, a diagnostic band appears near 1000 cm^{-1}.[44] It is found not only in salts of the

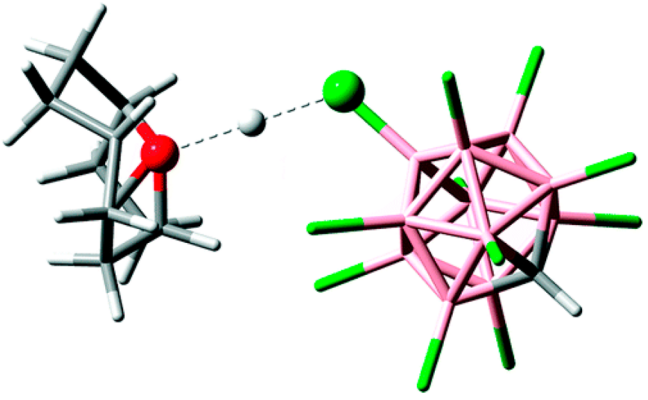


FIGURE 4. Graphical representation of the H-bond between the oxatriquinane cation and $H(CHB_{11}Cl_{11})$. Reprinted with permission from ref 36. Copyright 2012 American Chemical Society.

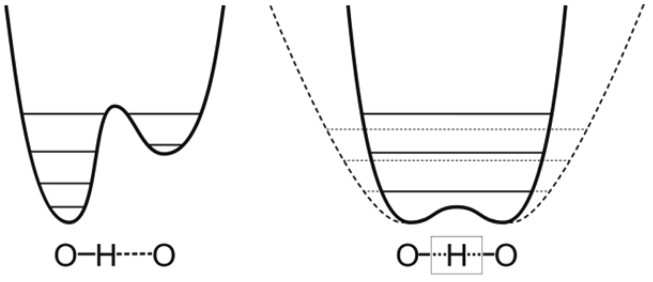


FIGURE 6. Proton potential energy diagrams illustrating (left) normal, unsymmetrical H-bonding and (right) short, strong, low-barrier (SSLB) H-bonding.

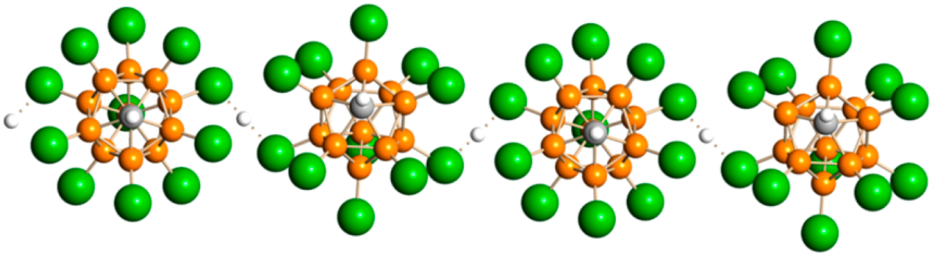


FIGURE 5. X-ray structure of the carborane acid $H(CHB_{11}Cl_{11})$ showing bridging, *di*-coordinate H^+ (white); green = Cl, orange = B, gray = C. Reprinted with permission from ref 39. Copyright 2006 American Chemical Society.

$H(OEt_2)_2^+$ ion, but also in proton disolvates of dimethylsulfoxide, nitrobenzene and tetrahydrofuran.[44] Its migration from 3296 cm^{-1} in Et_2OH^+(Xe) to 840 cm^{-1} in $H(OEt_2)_2^+$ as a function of disolvate symmetry, has been detailed in the gas phase.[49]

A poorly understood feature of the IR spectra of proton disolvates in condensed phases is that IR bands associated with groups adjacent to H^+, such as νCO in $H(Et_2O)_2^+$ or νCO and δCOH in $H(CH_3OH)_8^+$,[50] lose much of their intensity or disappear entirely.[51] This has been discussed in terms of delocalization of the proton along the essentially flat bottom of its potential well and is consistent with an indeterminate position of H^+ within an interval between the two O atoms. In a static description, this is equivalent to an extreme case of inhomogeneous broadening where neighboring chromophores are subject to a highly varied charge distribution and their absorption bands lose their definition. In a kinetic description, motion of the proton in the L−H^+−L moiety is fast on the vibrational time scale and produces rapid modulation of the force constants in neighboring vibrations. This issue becomes even more important in the IR spectrum of $H_{(aq)}^+$, discussed in section 5, where a continuous broad absorption (*cba*) appears across the entire IR spectrum.

4. Nature of $H(H_2O)_n^+$ in Organic Solvents

Most acid catalysis is carried out in polar organic solvents. What is the nature of an acid under these conditions? If the solvent is relatively polar and is rigorously dry, then the likely species is a disolvated cation, $H(solv)_2^+$, as described above. However, it is difficult to maintain solvents much drier than 10^{-4} M water during normal lab usage and, since water is more basic than most organic solvents, dissolved acids are likely to be hydrated. This does not necessarily mean they are ionized to $H(H_2O)_n^+$ cations. In wet dichloroethane, the strong NH-type acid bis(trifluoromethylsulfonyl) imide simply forms an H-bonded complex with water, $(CF_3SO_3)_2N{-}H\cdots OH_2$, rather than ionizing.[52] This contrasts with triflic acid which, although of similar acid strength, ionizes to $CF_3SO_3^-\cdots H_3O^+$ ion pairs. The difference can be understood in terms of anion polarizability and the specific geometry of the anion donor atoms. Ion pairing is the rule rather than the exception when considering ionized acids in organic solvents. This can be deduced from the sensitivity of the IR spectra of solutions of $H(H_2O)_n^+$ salts to anion variation in the following.

H_3O^+ (Eigen Ion). Conditions for the existence of the C_{3v} H_3O^+ ion are much more exacting than previously appreciated and the IR criteria used for three decades for its identification have been shown to be incorrect.[53] For H_3O^+ to be present, there must be a linear dependence between the frequencies of ν_{max}(OH) and $\delta(OH_3)$ within the ranges 3010−2536 cm^{-1} for ν_{max}(OH) and 1597−1710 cm^{-1} for $\delta(OH_3)$. H_3O^+ is *always* trisolvated with solvent molecules or weakly basic anions via three H-bonds. One novel structure of the H_3O^+ ion is that in $[H_3O\cdot 3C_6H_6][CHB_{11}Cl_{11}]$ whose X-ray structure shows three O−H$\cdots\pi$ hydrogen bonds (Figure 7).[54] The O−H bonds are directed toward π electron density just inside of the C_6 ring, not at its center. This interaction explains why low-*n* $H(H_2O)_n^+$ carborane salts have a useful degree of solubility in arene solvents, despite low solvent permittivity. Outside of the range of solvent basicity bound at the lower end by chloroalkanes and the upper end by water or tributyl phosphate, and with anions that do not meet the stringent requirements of weak basicity, low polarizability and high chemical stability, lower symmetry species are formed. One H-bond from H_3O^+ to the surrounding bases becomes stronger than the other two and for bases (B) stronger than tributyl phosphate, $H_2O{-}H^+{-}B$ type species are formed that are more closely related to the $H_5O_2^+$ ion than to H_3O^+.

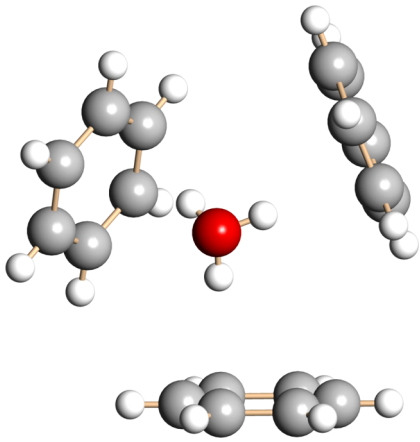


FIGURE 7. Perspective view O−H$\cdots\pi$ H-bonding in the X-ray structure of the cation in $[H_3O\cdot 3C_6H_6][CHB_{11}Cl_{11}]$.[54]

$H_5O_2^+$ (Zundel Ion). Like the H_3O^+ ion, the $H_5O_2^+$ ion is only formed under selected conditions of water concentration and particular strong acids, such as carborane acids. It is the favored ion for a number of strong acids in wet acetonitrile.[55] In our experience, this ion is always tetrasolvated with traditional H-bonds from the four terminal OH groups, that is, $H_5O_2^+\cdot 4Solv$. One early structure, trapped in a cryptand, has four solvating water molecules, making a $H_{13}O_6^+$ ion that is best formulated as $H_5O_2^+\cdot 4H_2O$.[56] In most solid state structures, however, H-bonds to the counterion replace most or all of the solvent molecules. For example, $[H_5O_2^+\cdot C_6H_6][CHB_{11}Cl_{11}^-]$ has one O−H$\cdots\pi$

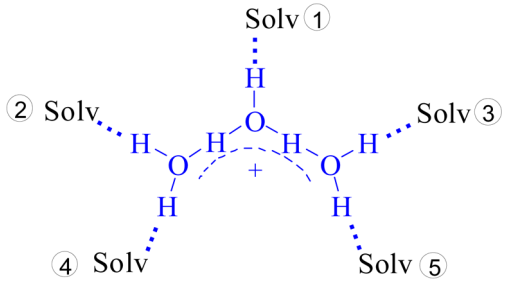


FIGURE 8. $H_7O_3^+$ ion core typical of $H(H_2O)_n^+$ in organic solvents plus additional H-bonding to as many as five solvent molecules (or anion donor atoms). Reprinted with permission from ref 58. Copyright 2008 American Chemical Society.

interaction with benzene and three O−H···Cl interactions with the carborane anion.[57]

As with the HL_2^+ proton disolvates discussed in section 3 above, the most distinctive feature of the IR spectrum of the $H_5O_2^+$ ion is the broad, low-frequency νOHO band at ca. 1000 cm^{-1} arising from the central, short, strong, low-barrier (SSLB) H-bond.[57] Its quantum nature has been studied in the gas phase.[49] The other distinctive feature of the IR spectrum of the $H_5O_2^+$ ion, in condensed phases, is the disappearance of the δH_2O band. As discussed above, the broadening or disappearance of bands in all HL_2^+ species having SSLB H-bonds can be understood in terms of the motion and indeterminate position (i.e., distribution) of the bridging proton in its essentially flat-bottomed potential well.

$H_7O_3^+$ Ions. Contrary to general expectation and data from gas phase experiments, neither the trihydrated Eigen ion, $H_3O^+\cdot(H_2O)_3$, nor the tetrahydrated Zundel ion, $H_5O_2^+\cdot(H_2O)_4$, is a good representation of H^+ when acids ionize in wet organic solvents, that is, the common condition of solvents in most acid-catalyzed chemistry, where the water concentration produces $H(H_2O)_n^+$ ions for $n > 3$. Rather, the core ion structure is $H_7O_3^+$ (Figure 8).[58] This finding reflects the unfortunate fact that perceptions regarding the nature of the aquated proton in solution have, over the past three decades, become too biased by calculations and by experiments in the gas phase, where counterions are absent. The obligatory presence of a counterion in solution, no matter how weakly coordinating, exerts an anisotropic electrostatic influence on $H(H_2O)_n^+$ cations that has been largely ignored. Prevalent ion pairing drives the structure away from the higher symmetry Eigen- and Zundel-type ions, that is, with H^+ delocalized over one or two water molecules, toward the $H_7O_3^+$ ion where H^+ is delocalized over *three* water molecules. The overall positive charge can influence up to five additional solvating molecules via H-bonding.

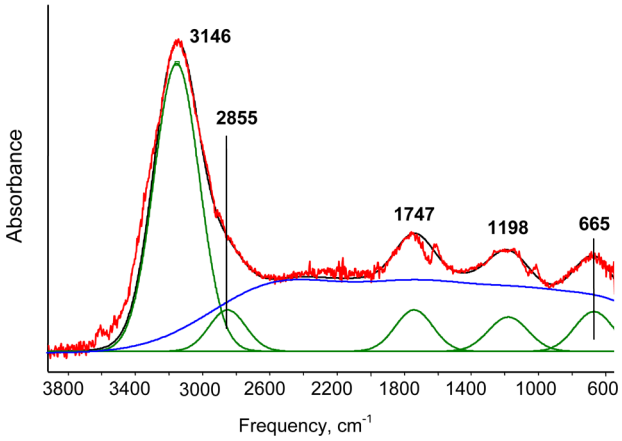


FIGURE 9. IR spectrum of $H(aq)^+$ (red) and its deconvolution into five bands (green) plus an underlying continuous broad absorption (blue). The points of inflection in the red spectrum near 1630 and 1050 cm^{-1} are artifacts. Reprinted with permission from ref 17. Copyright 2010 American Chemical Society.

The $H_7O_3^+$ ion has its own unique and distinctive IR spectrum that allows it to be distinguished from alternate formulations of the same stoichiometry, namely, $H_3O^+\cdot 2H_2O$ and $H_5O_2^+\cdot H_2O$.[58] It has its own particular brand of low-barrier H-bonding involving the 5-atom O−H−O−H−O core and it has somewhat longer O···O separations than in the $H_5O_2^+$ ion. Because of its core symmetry, the five peripheral O−H bonds offer three distinct sites for H-bonding to solvents, water and counterions. The central OH site of the C_{2v} O−H−O−H-O framework (labeled 1 in Figure 8) has the highest affinity for H-bonding, a consequence of being closest to the center of positive charge.

5. The Unique Structure of H^+ in Water

The first question to be answered about the "excess proton" in water is the extent of influence of positive charge, that is, how many water molecules solvate H^+? Because the subtraction of background water solvent from the IR spectrum of $H(H_2O)_n^+$ is difficult, this fundamental question had not been seriously addressed before. From exacting difference IR spectroscopy,[17] the answer is *six*. This means that $H_{(aq)}^+$ is a $H_{13}O_6^+$ ion. This immediately rules out an Eigen ion formulation where symmetry requires $H_9O_4^+$ or $H_{15}O_7^+$ stoichiometries. A tetrahydrated Zundel ion of formula $H_5O_2^+\cdot 4H_2O$ begins to look more viable, but IR spectroscopy and X-ray crystallography indicate something unique and different.

The IR spectrum of $H_{(aq)}^+$ is shown in Figure 9 (red).[17] The five band spectrum (green deconvolution) is notably simple, consistent with a highly symmetrical species. It is distinctly different from that of Eigen-type species.[18] One band is

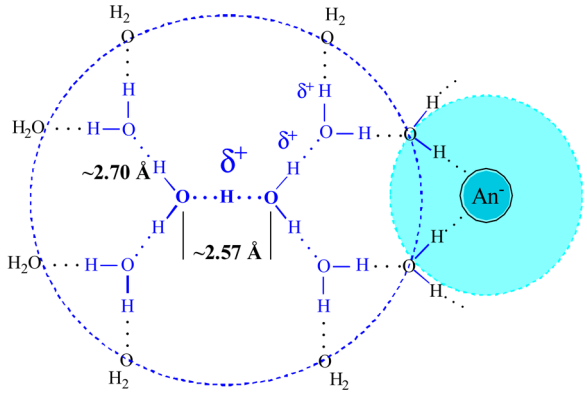


FIGURE 10. Structure of the $H_{13}O_6^+$ ion with a long central O···H⁺···O distance representative of H(aq)⁺. Typical ion-pairing is also shown. The dashed blue circle indicates the extent of positive charge delocalization. Reproduced from ref 18 by permission of The Royal Society of Chemistry.

missing, the δH_2O band, indicating low barrier H-bonding is present. There is some resemblance to Zundel-type species but the so-called "Zundel marker band", associated with the central νOHO band, has an anomalous frequency that suggests a *longer* central O···O separation than those in typical SSLB $H_5O_2^+$ tetrasolvates (2.39−2.45 Å). The X-ray crystal structure of $H(CHB_{11}I_{11})\cdot 8H_2O$, which is made up of nanotubes of $H_{(aq)}^+$ enclosed by cylindrical walls of $CHB_{11}I_{11}^-$ anions,[59] provides the only existing model for the structure of the $H_{13}O_6^+$ ion in liquid water. It shows an $H_{13}O_6^+$ ion with a central O···O separation of 2.57 Å. Such a long distance is unprecedented in a symmetrical species. It appears to be a function of the high degree of hydration of H^+ in this particularly crystal, making it more like liquid water than in any previous X-ray structure.

Thus, IR and X-ray data indicate that the structure of $H_{(aq)}^+$ is the unique $H_{13}O_6^+$ ion shown in Figure 10. It should be named the Stoyanov ion after my collaborator who carried out all the meticulous IR work to establish its nature experimentally. It differs from the structure favored by theory that treats $H_{(aq)}^+$ as a charge defect[60] and which, in adopting a distorted Eigen ion structure, reproduces neither the present IR spectrum nor the long O···O distance.

A particularly interesting and unique part of the IR spectrum of $H_{(aq)}^+$ is the continuous broad absorption (*cba*) shown in Figure 9 (blue).[18] This distinctive *featureless plateau* spreads across nearly the entire IR frequency range and is not the same as the broad so-called ABC features[61] seen in other H-bonded systems.[62] The *cba* is clearly a manifestation of unique, low-barrier H-bonding within the unique *five*-H-atom core of the $H_{13}O_6^+$ Stoyanov ion whose proton dynamics are faster than the IR time scale. We estimate that the *cba* accounts for ca. 70% of the IR absorption of $H_{(aq)}^+$ at room temperature, the remaining 30% being manifest in the normal line spectrum (green in Figure 9). As expected, the ratio of the intensity of the *cba* to that of the line spectrum appears to get smaller with decreasing temperature.[63] The reproduction of these features creates an exacting test for theory.

What does it mean for reaction mechanisms when the proton dynamics in the $H_5O_2^+$ core of 70% of $H_{(aq)}^+$ ions are faster than the IR time scale? According to the Jencks principle,[64] eloquently enunciated by Cox,[65] a species cannot be an intermediate in a reaction if it does not exist on the IR time scale under the conditions of the reaction. For the purposes of the $H_{13}O_6^+$ ion, this means that H^+ is available instantaneously from its $H_5O_2^+$ core and the rate of H^+ transfer to any substrate will be dependent only on the time scale of Grotthuss proton hopping[66] through the outer solvation shell of the $H_5O_2^+$ core, that is, through one or two water molecules. Thus, mechanisms of proton transfer in aqueous solution should be written in terms of $H_{13}O_6^+$ or $H_{(aq)}^+$ but only one or two water molecules solvation of H^+ will appear in the rate equation. Ironically, this gives an accidental reality to mechanisms written in terms of Eigen (H_3O^+) or Zundel ($H_5O_2^+$) ions but the $H_{13}O_6^+$ description is the accurate identity of $H_{(aq)}^+$.

A final word on ion pairing. The dependence of the IR spectrum of $H_{(aq)}^+$ on the nature of the counterion, even with large, weakly coordinating anions such as carboranes, indicates that most fully ionized acids exist in aqueous solution as solvent-separated ion pairs.[18] This will come as a surprise to many since the high electrical conductivity of aqueous acids is typically equated with ideal (i.e., fully ionized) electrolyte behavior. It must be a consequence of the electrostatic fields of the ions and the ability of water to delocalize their charge via H-bonding.

This is the *sine qua non* of our findings. Liquid water provides a unique environment for H^+ that leads to greater mobility and delocalization of charge than previously suspected. Results from the solid state and the gas phase have been quite misleading with respect to the liquid phase.

6. Conclusion

Hydrogen bonding is everywhere, and acid/base concepts lie at the heart of most chemical reactions. As the lightest element, hydrogen shows more nonclassical, that is, quantum, behavior than any other element. It is no wonder that H^+ shows such complex chemistry. This Account has

summarized recent advances in the chemistry of acids and H-bonding in condensed media with the goal of providing realism to the descriptions of chemistry hidden under the often simplistic designations H^+, HA, H_2A^+, H_3O^+, and $H_5O_2^+$. For such a seemingly mature area of chemistry, our adventures have been more than interesting. They have changed the way we think about the proton and suggest some ways that myths can be removed from textbooks.

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BIOGRAPHICAL INFORMATION

Christopher A. Reed is Distinguished Professor of Chemistry at the University of California, Riverside. He was born in New Zealand and educated at The University of Auckland. After postdoctoral studies at Stanford University in 1971−1973, he joined the faculty at the University of Southern California and spent 25 years there. In 1998, he moved to University of California, Riverside, to create the Center for *s* and *p* Block Chemistry. His current research focuses on reactive cations across the periodic table. Earlier research interests included organotransition metal chemistry, the bioinorganic chemistry of iron porphyrins and copper proteins, spin−spin coupling phenomena, fullerene redox chemistry, and supramolecular assembly.

FOOTNOTES

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The authors declare no competing financial interest.

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