Proton Solvation and Proton Mobility

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(Received 21 September 1999; accepted in revised form 13 November 1999)

Abstract. Experimental evidence for proton solvation and proton mobility is analyzed and the results are compared with recent simulations. Three factors contribute to differences in proton solvation energies: hydrogen-bond cleavage, changes in hydrogen-bond lengths, and proton delocalization. These factors are estimated from experimental attributes. In dilute acidic aqueous solutions \( \text{H}_2\text{O}^+ \) is more stable than \( \text{H}_3\text{O}^+ \) by about 0.6 kcal/mol. This estimate, together with the activation energy for proton mobility, supports the \( 121 \) mechanism for proton mobility in which a protonated water monomer is transformed, by second-shell hydrogen-bond cleavage, to a protonated dimer and back to another protonated monomer.

INTRODUCTION

Structure and dynamics are distinct concepts in chemistry, yet intimately related. In the field of proton transfer reactions this has been realized early on, and relations connecting rate and equilibrium constants in this family of reactions are well documented. Generally, a perturbation which stabilizes the reactants slows down the reaction, whereas stabilization of the products will speed it up. Proton mobility in liquids (most notably, water) may be conceived as a sequence of proton transfer reactions. The product of one step is necessarily the reactant for the next step. Hence, if any intermediate along this sequence was exceedingly stable, it would serve as a trap which would slow down further proton movement. Thus, unlike a single-step reaction, this multi-step process could be fast only if all the intermediates are roughly isoenergetic. Since protons move exceptionally fast in water, almost five times faster than any other cation, we expect to identify several nearly isoenergetic protonated water structures along the proton migration coordinate.

Two candidates for protonated water structures, which might participate in proton mobility, are the (aquated) \( \text{H}_2\text{O}^+ \) and \( \text{H}_2\text{O}_2^+ \) cations, sometimes known as the \( \text{Eigen}^8 \) and \( \text{Zundel}^9 \) cations, respectively. The nature of the “correct” form of protonated water was extensively debated. Unfortunately, from the spectroscopy of dilute acidic solutions it is difficult to address this question, and all that may be stated with relative certainty is that in \( \text{concentrated} \) acidic solutions \( \text{H}_2\text{O}^+ \) becomes the dominant species. This has been recently demonstrated by Kameda and coworkers using both X-ray and neutron diffraction techniques.

In a recent series of papers it was claimed that in dilute aqueous acids the Eigen cation is more stable, but the Zundel cation is nearly isoenergetic with it. Proton mobility is a periodic isomerization reaction (Fig. 1), in which the solvation state of the proton cycles between these two structures. The rate-limiting step for the Eigen \( \rightarrow \) Zundel transition is suggested to be the cleavage of a second-shell hydrogen-bond (HB).

At the same time, several groups are actively involved in simulating both proton mobility and its solvation structures by classical and quantum molecular dynamics techniques. Several of these works are represented in this special issue, as well as simulations of proton migration in biological proton wires. Interestingly, most of the simulations have suggested that, quantum-mechanically, it is the Zundel cation which is stable.


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Fig. 1. The suggested mechanism of proton mobility involves cleavage of the b-a hydrogen-bond, followed by formation of the corresponding a-c bond. Hydrogen atoms: small black spheres; protonated oxygen atoms: large white spheres; unprotonated oxygens: large gray spheres.

more stable. Thus if proton mobility is to occur through cleavage of a second-shell HB, it involves the reorganization of one Zundel cation to another. It is only very recently that some of the simulation work conceded that in room-temperature water, the Eigen cation is indeed slightly more stable than the Zundel cation.

The major issues pertaining to the complex problem of proton solvation and proton mobility are summarized in an insightful commentary by Hynes. Here, the relevant experimentally-motivated arguments are reviewed and extended, particularly in conjunction with the thermodynamic properties of water and their relation with the variable hydrogen-bonding patterns in water. The conclusions are compared with the evolving simulation results of the past five years.

PROTON SOLVATION
This section updates the previous experimentally-motivated estimates of the relative stabilities of the Eigen and Zundel cations ($H_2O^+$ and $H_2O_2^-$, respectively) in liquid, room-temperature water. Imagine an Eigen cation centered at oxygen a, denoted $O_a$. It has three first-shell water ligands whose oxygens are nearly all 4-coordinated (e.g., $H_2O_4^-$). Consider a transformation which converts it into a Zundel cation,

$$(H_2O_4^-) \rightarrow (H_2O_2^-)_2 = H_2O^+ - H^+ - O_a - H_2O^+ - (OH_2)^+ + H_2O$$

(1)

demonstrated in the upper part of Fig. 1. One of the first-shell oxygens, say $O_a$, reduces its coordination number to 3. Consequently, the (average) bond lengths (and bond angles) readjust, and the proton delocalizes over the 2-oxygen center ($O_a - O_b$) of $H_2O_2^-$, forming the short "special bond", $O_a - H - O_b$. It is therefore conceivable that three factors contribute to the free energy difference:

- Cleavage of a second-shell hydrogen bond;
- Hydrogen-bond length changes;
- Delocalization entropy.

Hydrogen-bond Cleavage
The first, and most energetically costly step in the Eigen $\rightarrow$ Zundel conversion, is the cleavage of a second-shell HB, most likely by HB bending, which is coupled to water librations. Unlike first-shell HBs around the protonated water core, $H_2O_4^-$, which are considerably stronger than in bulk water, it is assumed that the second-shell bonds (to $H_2O_4^-$) are already of comparable strength to those in the bulk.

The HB strength in room-temperature liquid water has been determined by several spectroscopic methods, such as Raman scattering, near-infrared spectroscopy, and depolarized light scattering. According to these studies, the HB strength is in the range 2.4-3.6 kcal/mol. The value adopted here is 2.6 kcal/mol.

Parenthetically, a more familiar value for the $OH^--O$ bond strength is 4.5-5.5 kcal/mol. It represents the HB well-depth of water potentials employed since the early classical molecular-dynamics simulations of liquid water. Evidently, classical mechanics does not include the zero-point energy effect, which is substantial for HBs. A quantum-mechanical simulation of liquid water indeed shows a smaller value for the HB strength than in the classical case, but a detailed theoretical analysis of the HB strength in liquid water is still lacking. As will be argued below, the zero-point energy is also the major quantum-mechanical effect for the solvated proton.

In this respect, recall that Pauling, in his seminal monograph, has also suggested a HB strength of 5 kcal/mol, about half the vaporization enthalpy of water. The accidental agreement between these two numbers precipitated a misunderstanding of the HB strength that would last for many years. Indeed, it is a rather
extreme assumption that most of the water–water interaction energy is due to nearest neighbors. If we adopt the spectroscopic value of 2.6 kcal/mol, then only about half of the vaporization enthalpy is due to hydrogen bonding. The remainder must then be ascribed to non-nearest neighbor interactions (and non-hydrogen-bonded interactions with nearest neighbors). Incidentally, a similar partition emerges from recent solvatochromic studies of excited hydroxyxyls, which ascribe about half of the spectral shift to specific HBs to the OH moiety; the rest is due to nonspecific dipolar interactions. If conclusions concerning hydrogen bonding are to be drawn from the enthalpy of a phase transition, one had better select a transition between two condensed phases in which the nonspecific interactions do not vary substantially. Such a strategy is adopted below.

Hydrogen-Bond Rearrangement

Following the cleavage of the second-shell HB in eq 1, extensive rearrangements follow. Assuming that the HB linearity is preserved, the predominant change is in HB lengths. One faces the challenge of estimating these changes in liquid water and their energetic consequences. While it is clear, both theoretically and experimentally, that the “special bond,” O––H–O, shortens to about 2.4 Å, the average lengths of the HBs formed with the Eigen and Zundel cations in liquid water are not precisely known. To estimate them, one may apply the Pauling-BEBO (Bond-Energy–Bond-Order) correlation to pairs of covalent O–H bonds with their adjacent H–O HBs.

In a family of covalently bonded A–B–C molecules, one often observes a correlation between the A–B and B–C bond lengths (say, r1 and r2). A perturbation which lengthens one bond shortens the other and vice versa. This behavior, which reflects electron density shifts between the two bonds, is described empirically by the BEBO concept of bond-order conservation, combined with Pauling’s bond-order definition, and

\[
\exp [- (r - r) / a + \exp [- (r - r) / a] = 1 \tag{2}
\]

Here, r is a “standard” bond-length and a is an empirical parameter.

This relationship has been applied to equilibrium structures observed in crystals of related compounds, as well as to unstable structures along the reaction paths on collinear A–B–C potential energy surfaces. For example, the predicted saddle-point geometries for HHHH triammonium (X – halogen) were shown to be in good agreement with ab initio calculations. The correlation has also been applied to HBs in ROH crystals (R = radical). For example, in the present issue it is applied to the triple proton transfer in crystalline pyrazoles.

Two bond-distance pairs are known for liquid water: the water–water interaction (H–O–HO) and the “special pair” in H2O2. These are points 1 and 4 in Table 1 and Fig. 2 (closed circles), which are used as “anchors” for the correlation. The correlation line (Fig. 2) passes through them with r1 = 0.9535 Å and r2 = 0.353 Å. The “standard” bond length, r, represents the shortest possible OH bond. The value chosen is just slightly shorter than that of an isolated water molecule in the gas phase (r1 = 0.956 Å)32. The value of a correlates nicely the bond orders, n = exp[-(r - r) / a], for oxygen–oxygen single, double, and triple bonds (n = 1, 2, and 3) taking r, as the single-bond length and using the atomic radii in Table 7-5 of ref 48.

In addition, the corresponding data for ice is also displayed on the figure (square). The O–H distance in ice Ih has been the subject of some dispute: older work assigned it a value of 1.01 Å, whereas Whalley27 presented several arguments which show that it is not much different from other forms of ice, around 0.985 Å. Together with a O–O distance of 2.76 Å, this data point falls close to the correlation line, whereas setting r = 1.01 Å will displace it well above the line. Hence the Pauling-BEBO correlation provides yet another argument favoring the smaller value of the O–H distance in ice Ih. This smaller value was finally explained by a model which incorporates oxygen disorder.24

Returning to the protonated water cations (gray circles in Fig. 2), one may now use the correlation to estimate their first-shell HB distances in the liquid phase. Bond distances from density functional theory

<table>
<thead>
<tr>
<th>structure</th>
<th>r_OH (Å)</th>
<th>r_O–O (Å)</th>
<th>ΔH°_f</th>
<th>(kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 HO–H–O</td>
<td>0.985</td>
<td>1.88</td>
<td>2.86</td>
<td>2.6</td>
</tr>
<tr>
<td>2 HO–HO</td>
<td>0.985</td>
<td>1.775</td>
<td>2.76</td>
<td>3.1</td>
</tr>
<tr>
<td>3 H2O2</td>
<td>1.01</td>
<td>1.63</td>
<td>2.64</td>
<td>3.7</td>
</tr>
<tr>
<td>4 H2O2−</td>
<td>1.04</td>
<td>1.49</td>
<td>2.43</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Supplementary text:

Sum of two previous columns (assuming linear HBs).

Fig. 2. The Pauling BERÖ correlation, eq 2, applied to the data of Table 1 for liquid water (circles) and ice Ih (square). The fitting parameters are \( r = 0.9535 \text{ Å} \) and \( \alpha = 0.353 \text{ Å} \).

(DFT) calculations\(^{51,52}\) were shown to obey the correlation,\(^{10}\) albeit with a somewhat larger value of \( \alpha \). Assuming that the covalent OH bond lengths are less sensitive to the details of the calculation, we take their average DFT values,\(^{10,13}\) 1.01 and 1.04 Å for the Zundel and Eigen cations, respectively. Post-Hartree–Fock ab initio calculations\(^{55}\) yield smaller values, 1.00 and 1.01 Å, but the larger value of 1.04 Å agrees with neutron diffraction from concentrated HCl.\(^{53}\)

The corresponding O–O distances are consequently gotten from points 2 and 3 on the correlation curve in Fig. 2: 2.64 and 2.53 Å for the Zundel and Eigen cations, respectively. Hence, in the Eigen → Zundel transformation, five HBs change their average lengths, and these are summarized in Scheme 1. As seen in the scheme, the “special bond” shortens from 2.53 to 2.39 Å, the two other O–O distances lengthen from 2.53 to 2.64 Å, while the two bonds to O₆ shrink from their near bulk-water value, 2.84 Å, to 2.64 Å. (The second-shell HB length is taken as 2.84 Å, just slightly shorter than the 2.86 Å of bulk water.) Summing these five distance changes we obtain an overall change of -0.32 Å. (Applying the average DFT HB distances,\(^{51,55}\) a previous work\(^{19}\) estimated an overall change of 0 Å.)

It remains to translate the overall decrease in bond length to energetic stabilization. Several arguments support the estimate\(^{14}\) of 5 kcal/mol per 1 Å change in the HB length, summarized by the expression

\[
\Delta H_{\text{OH–O}} = 2.6 - 5\Delta r_{\text{O–O}} \tag{3}
\]

which relates the standard enthalpy of the HB (in kcal/mol) with the deviation (in Å) of the oxygen–oxygen distance from its value in water. Most of the arguments below are based on thermodynamic properties of water and ice (see Table 1 in ref 75) and, concomitantly, provide them with an interpretation in terms of HB cleavage and readjustment.

(i) The specific heat of water is about 1 cal/deg g for 0.36 kcal/mol per 20 °C. This value may be ascribed to the two effects discussed above, namely, cleavage and shortening of HBs. A Raman study shows that 5% of the HBs break upon 20 °C heating (Table 3 in ref 39). Given a HB strength of 2.6 kcal/mol,\(^{29}\) and 2 bonds per water molecule, this amounts to 0.26 kcal/mol. The remainder, 0.1 kcal/mol, is thus ascribed to HB shortening.

X-ray studies over an extended temperature range\(^{35-37}\) show a shift of about 0.01 Å per 20 °C in the first peak of the radial distribution function for water. The following linear temperature dependence has been deduced:

\[
r_{\text{O–O}} = r_{\text{O–O}}^0 + \alpha (T-273) \tag{4}
\]

Based on the X-ray data of Narten, Scatts et al.,\(^{36}\) suggest that \( r_{\text{O–O}}^0 = 2.835 \text{ Å} \) and \( \alpha = 5.2 \times 10^{-4} \text{ Å}^{-1} \), whereas Corban and Zeidler\(^{37}\) have \( r_{\text{O–O}}^0 = 2.814 \text{ Å} \) and \( \alpha = 4.293 \times 10^{-4} \text{ Å}^{-1} \). Thus 20°C = 0.01 Å is a reasonable compromise. Assuming two HBs per water molecule, the lengthening of each HB costs 0.1/(2 x 0.01) = 5 kcal/mol per Å.

(ii) The melting enthalpy of ice at 0 °C is 1.44 kcal/mol. This value is again ascribed to a combination of HB cleavage and shortening. The Raman study of Walrafen et al.,\(^{39}\) estimated that about 16% of the HBs are broken in 0 °C water (Table 3 there). A random network model for liquid water\(^{26}\) suggests that 13.5% of the HBs are broken at 10 °C which, using the previous estimate (5% per 20 °C), gives 11% at 0 °C. Here, we assume that 10% of the HBs break during the melting process.

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Since the HB strength at 4°C is 2.7 kcal/mol, cleavage of 10% of the HBs in 1 mole of water (2 moles of HBs) consumes 2 x 0.1 x 2.7 = 0.54 kcal/mol. The remainder, 0.9 kcal/mol, is ascribed to 0.09 Å HB lengthening, from 2.76 Å in ice to 2.85 Å in 4°C water, resulting in the same estimate as above. It is interesting to note that during the melting process most of the latent heat is consumed by HB lengthening, while during heating of liquid water their cleavage becomes the dominant process.

(iii) The isotope effect on the enthalpy of melting may be estimated by assuming that the dominant effect on the HB strength, which is 0.2 kcal/mol stronger in D₂O than in H₂O. This assumption is corroborated by the isotope effect on the vaporization enthalpy, which is 0.4 kcal/mol (10.7 kcal/mol for H₂O vs. 11.1 kcal/mol for D₂O), exactly twice the difference in HB strength. If 0.54 kcal/mol is consumed by HB cleavage upon melting of H₂O ice (as before), then an additional 0.2 x 2.7 x 0.54 = 0.04 kcal/mol is required to melt D₂O ice. Its enthalpy of melting becomes 1.44 + 0.04 = 1.48 kcal/mol, as compared with an experimental value of 1.50 kcal/mol. This consistency check verifies the conclusion in (ii) that about 0.9 kcal/mol is consumed by stretching of HBs upon melting of ice.

(iv) From the difference in HB length between water and ice, one estimates the HB strength in ice to be 3.1 kcal/mol, in agreement with some old Raman data. The first minimum in the radial distribution function of water occurs around 3.4 Å, and that is usually considered as a completely broken HB. Linear extrapolation from a 2.86 Å bond using eq 3 suggests total cleavage (ΔH_f(0)-0) at 3.38 Å. This is in excellent agreement with the location of the first minimum.

Having validated eq 3, one is in a position to use it for estimating the HB strength for all the structures appearing in Table 1. Implicit is the assumption that this relation extends from (neutral) bulk water to the various protonated forms of water, an assumption supported by the fact that these fall on the same line in Fig. 2. The estimated enthalpies are given in the last column of Table 1. Note the “extra-strong” HBs to the H₃O⁺ moiety (4.3 kcal/mol). A similar trend is observed, qualitatively, also in protonated gas-phase water clusters: first-shell HBs are considerably stronger. Evidently, the gas-phase enthalpies are considerably larger than the HB strength cited in the table because finite-size clusters are involved. The HB enthalpies deduced here correspond to a small reorientation of the hydrogen-bonded molecules within the dielectric environment of all other water molecules. Nevertheless, the qualitative trend is the same in both cases, and it plays a major role in the elucidation of the proton mobility mechanism.

Finally, the relative stability of the Eigen and Zundel cations is obtained from the total HB conformation, 0.32 Å obtained above, and its energetic cost according to eq 3. Hence 0.32 x 3 = 0.9 kcal/mol is the relative stabilization of the Zundel cation due to HB rearrangement. Since its preparation from the Eigen cation required the cleavage of one HB at the investment of 2.0 kcal/mol, it is enthalpically only 1.0 kcal/mol less stable than the Eigen cation. Qualitatively, therefore, the conclusion is the same as before, but with a revised energy difference.

**Delocalization Entropy**

Estimating the free energy difference between the two cations requires knowledge of the entropic contribution, ΔS°. The main effect is that in the Eigen cation the proton is localized to a single oxygen center, whereas in the Zundel cation it delocalizes over two such centers. This could amount to an additional energetic stabilization of

\[ TΔS° = RT \ln 2 = 0.4 \text{ kcal/mol} \]  

at T = 300 K, provided that the proton zero-point energy is higher than the barrier separating the two minima in a fluctuating H₃O⁺. The above value is in very good agreement with recent quantum simulations. This could indicate that the dominant quantum effect is that of zero-point energy, which allows the proton to delocalize between the two oxygen centers of H₃O⁺.

In terms of free energy, the Zundel cation is therefore only 0.6 kcal/mol (about RT) less stable than the Eigen cation. Most simulation work has initially reached an opposite conclusion, reversing the understanding of generations of electrochemists, as verified by early ab initio calculations, which the proton is localized on a single water molecule. The situation has changed again with the recent multisite empirical valence bond (MS-EVB) work of Schmitt and Voit, who find that the Zundel cation is less stable by 0.38 kcal/mol. This agrees nicely with the present estimate (0.6 kcal/mol). A similar work of Vuilleumier and Borgis still concludes that the Zundel cation is more stable, a discrepancy which could be attributed to differences in the MS-EVB potential parametrization (most notably, the exchange integrals). In the recent simulations of both Marx et al. and Zahn and Brickmann, the solvated proton resembles H₃O⁺ most of the time.

**PROTON MOBILITY**

The traditional views on proton mobility are summarized in many places, for example, in the monograph of Erdey-Grúz. While one may be im-

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pressed with the often conflicting viewpoints expressed
in the literature, the dominant interpretation delineates
from the works of Bernal and Fowler,84 Conway et al.,85
and Eigen and coworkers.86-88 This is also what one
usually finds in textbooks.89 The abnormally large value
for the proton diffusion coefficient, 9.3 × 10^-5 cm^2/s at
300 K,7,83 is supposed to contain two contributions: the
minor one is due to hydrodynamic diffusion of H_2O^+
("vehicle mechanism")90,91 occurring with the same dif-
fusion coefficient as that of water, 2.3 × 10^-5 cm^2/s.90,91 The
major contribution (the "excess mobility") is due to a
chain of proton hops, from the edge of a hydrogen-
bonded water cluster (over which the proton delocali-
izes) to an adjacent water molecule which reorients,
in the first solvation shell of the H_2O^+ ion, in order to
accept the incoming proton.

These views should be examined in light of the ener-
gies of proton solvation and proton mobility. Proton
solvation has already been discussed. The second as-
pect is summarized in Fig. 3, which shows the activa-
tion energy, E_a, for proton and hydroxide ion mobility
and for water self-diffusion. To obtain it, the experi-
mental diffusion coefficients, D,90,91 were plotted as D vs. 1/T
and fitted to a sixth order polynomial, which was then
differentiated analytically. Focusing on the data near
room temperature, one notes that E_a for proton mobility
is 2.5 kcal/mol, whereas for water self-diffusion it is
twice as large.

A different route for obtaining activation energies for
proton mobility involves measurements of proton trans-
fer between H_2O^+ and H_2O, using ^17O NMR relaxation
measurements.92-94 These studies agree nicely with
those of proton mobility giving, at room temperature,
E_a = 2.4-2.6 kcal/mol, although E_a does not seem to
vary with temperature as in Fig. 3. For hydroxide trans-
fer, the NMR data are quite scattered,92-94 some above
and some below the activation energy for proton mobility,
a situation which has provoked debates in the literature.95

The three basic assumptions of the traditional ap-
proach, namely, the involvement of first-shell water
rotation, extensive proton delocalization, and hydrody-
namic transport, contradict the experimental data of
Fig. 3, as explained below.

Water Rotation

Water rotation in the first solvation shell of H_2O^+
cannot be the rate-limiting step for proton mobility since
it requires at least one first-shell HB to be broken. These
bonds (estimated above at 4.3 kcal/mol) are much stron-
ger than bulk HBs (2.6 kcal/mol), and the energy re-
quired for their cleavage far exceeds the experimental
activation energy for proton mobility. (The activation
energy for water molecule rotation in bulk water has

![Fig. 3. Experimental activation energies for proton and hydroxide mobility (solid line) and water self-diffusion (dashed line) as a function of inverse absolute temperature.](image)

also been measured,96 and it already exceeds that of
proton mobility). In contrast, second-shell HBs may
have bond energies close to those in bulk water. Cleav-
age of a second-shell bond could thus account for the 2.5
cal/mol activation for proton mobility.

Proton Delocalization

In order for the proton to delocalize on a hydrogen-
bonded water cluster, H^+\(\cdot\)(H_2O)_n, all the N water mol-
eules in the cluster should be triply coordinated. N = 1
denotes a proton localized on a single water molecule,
H_2O^+. It forms three HBs with first-shell water ligands.
N = 2 is a proton delocalized on a water dimer, H_2O_2^+.
In addition to the central "special" bond, each oxygen don-
ates two HBs and is thus triply coordinated. As we
have seen above, the transition from N = 1 to N = 2
involves cleavage of one HB, at the cost of 2.6 kcal/mol,
which is partly compensated by HB rearrangement
and delocalization entropy. Yet, according to the estimate
in the previous section, the transition is uphill by 0.6 kcal/
мол. To increase N by one additional unit requires
breaking one additional HB because the coordination
number of room-temperature water is close to four. In
the limit of large N, the compensating factors become
negligible because the charge is already delocalized
over many oxygen atoms. Not only is increasing the
cluster size an uphill process, but the energy penalty for
it increases with N. The probability of observing large
protonated water clusters must therefore decay rapidly
with increasing N.

Historically, it was Eigen who, following proton mo-

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ize over large hydrogen-bonded clusters. This apparently contradicts the prevalence of the Eigen cation, the most localized form of protonated water. It is now accepted that protons migrate slower in the nearly perfect HB network of ice than in the random network of liquid water. The motivation for assuming fast proton motion within large water clusters is gone (unless they are tripoly coordinated and rearranged as in proton-wires), yet many textbooks (incorrectly) retain this concept as an important aspect of the Grothuss mechanism in liquid water.

Hydrodynamic Transport

Does about 1/3 of the proton mobility occur by diffusion of the water molecule to which the proton is attached? As Fig. 3 shows, the activation energy for water self-diffusion is twice that of proton mobility, requiring the cleavage of two HBs (or involving a sizeable non-hydrogen-bonded component). This refers to an uncharged water molecule. The activation energy for translational diffusion of H_2O should be even larger, because of its extra-strong first-shell HBs. Since E_a is only 2.5 kcal/mol, a water molecule as a vehicle probably contributes only negligibly to proton mobility at room temperature.

MODERN PROTOTROPIC MECHANISMS

The concepts underlying the modern prototropic mechanisms have been briefly reviewed by Hynes. These will now be confronted with findings of recent molecular-dynamics simulations as manifested in this issue of the Israel Journal of Chemistry. A major conclusion from the above discussion is that the rate-limiting step for proton migration in room-temperature water is the cleavage of a second-shell HB. This conclusion has been reached independently in refs 17 (experimental arguments) and 21 and 22 (simulations). A similar step of HB cleavage has been observed in an ab initio calculation of acid dissociation by Ando and Hynes.

Unfortunately, the ab initio simulations of refs 21 and 22 could only be propagated to a few picoseconds, so direct observation and analysis of the HB-cleavage step was difficult to achieve. An interesting check of this prediction is reported in the article by Vulecmeier and Borgis. Using the computationally less demanding MS-EVB method, they could monitor proton translocation events from one H_3O^+ moiety (H_2O-H_2O-H_2O) in their case, to another (H_2O-H_2O-H_2O). At the same time they have monitored the coordination numbers of O and O; the first is expected to decrease from 4 to 3, whereas the second is expected to increase from 3 to 4. The suggested coordination number changes could be verified only partially; the results depend on the geometric parameters defining the HB. For some parameters there were no obvious changes in the coordination numbers, whereas for others predominantly HB formation was seen. This might be due to the fact that the Zundel (and not Eigen) cation is the most stable in these simulations.

Indeed, within the family of “Moses mechanisms”, in which second-shell HBs cleave in front and reform behind the migrating proton, one can identify several submechanisms. If the Eigen cation is the most stable one, the predicted mechanism is (6)

\[ H_2O^+ + H_2O \rightarrow H_2O^- \rightarrow H_2O^+ + H_2O \]  (6)

(see Fig. 1). In eq 6 an abbreviated notation is adopted, displaying explicitly only the cluster of tripoly coordinated water molecules, H_2O, over which the proton delocalizes (and not the water molecules hydrogen-bonded to it). In terms of the size (N) of this cluster, eq 6 represents a “121 mechanism”. It involves an Eigen cation (N = 1) which, by virtue of a second-shell HB cleavage (eq 1), is momentarily converted to a Zundel cation (N = 2) which, by formation of a HB (to O), in eq 1 is converted to another Eigen cation (N = 1).

If, however, it is the Zundel cation that is the most stable, one may envision two different mechanisms

\[ H_2O^+ + H_2O \rightarrow H_2O^- + H(OH)H \rightarrow H_2O^+ + H_2O^+ \]  (7a)

\[ H_2O^+ + H_2O \rightarrow H_2O^- + H(OH)H \rightarrow H_2O^+ + H_2O^+ \]  (7b)

The first may be termed a 212 mechanism; it involves first HB formation, which localizes the proton to the remaining tripoly-coordinated oxygen atom. Subsequently, a HB cleavage event regenerates another Zundel cation. The second is a 232 mechanism; it begins with a second-shell HB cleavage which converts H_2O^+ to H_2O and then, by HB formation, back to another Zundel cation. It is not clear which of these two mechanisms actually occurred in the simulations of refs 22 and 32.

In addition to the thermodynamic arguments for the 121 mechanism (eq 6), there might also be a kinetic reason for its prevalence over 2n2 mechanisms emanating from the Zundel cation (eq 7). In the latter case, reaching the transition state requires not only the cleavage of a HB, but also sacrificing the proton delocalization energy, eq 5. The activation energy for the 2n2 mechanisms might then be around 3 kcal/mol, higher than the experimental value of 2.5 kcal/mol. In contrast to previous simulations, a recent path-integral/ab initio simulation endorses a 121 mechanism as the most likely scenario for proton mobility in liquid water.
CONCLUSION
Proton mobility is intimately connected to proton solvation. The connection is predominantly through hydrogen-bonding, which determines the relative stability of protonated water clusters. However, it is insufficient to take into account only the fraction of broken HBs (2.6 kcal/mol per bond). Small changes in HB lengths, which occur near protonated water clusters, play an important role in determining their relative energetics.

Estimating these effects from experimental data is not an easy task. First, the empirical Pauling-BEBO correlation was applied to estimate the HB lengths in the first solvation shell of $\text{H}_2\text{O}^+$ and $\text{H}_2\text{O}^2$. Then, using a combination of thermodynamic properties of water with X-ray and Raman data it was concluded that the OH--O bond becomes stronger by about 5 kcal/mol for every 1 Å of contraction. This gave a simple explanation for the heat capacity and freezing enthalpy of water, and made it possible to estimate the relative stability of the two protonated water cations in liquid water: $\text{H}_2\text{O}^+$ is more stable than $\text{H}_2\text{O}^2$ by about 1 kcal/mol. Taking into account additional stabilization of $\text{H}_2\text{O}^2$ due to proton delocalization over the two oxygen atoms (the largest water cluster over which noticeable delocalization occurs), the energy difference between the two cations reduces to only 0.6 kcal/mol.

The existence of two nearly isoenergetic protonated clusters in liquid water is a key for understanding the exceptionally rapid proton mobility, which is postulated to involve a periodic transformation from one structure to the other. By breaking a second-shell HB, the protonated monomer ($\text{H}_2\text{O}^+$) is converted into a protonated dimer ($\text{H}_2\text{O}^2$). In this dimer, the proton is equally shared by the two oxygen atoms so that no additional energy is required to promote proton transport. This explains the relatively low activation energy for proton mobility, 2.5 kcal/mol in room-temperature water. Subsequent formation of a HR localizes the proton on the other oxygen atom of the dimer, completing the hopping step. This 121 (monomer $\rightarrow$ dimer $\rightarrow$ monomer) mechanism is the basic process accountable for the normally fast proton mobility. The alternative 212 mechanism not only contradicts the analysis of proton solvation (from which $\text{H}_2\text{O}^+$ emerges as the more stable species), but also results in an activation free energy which, due to loss of proton delocalization, should be 0.4 kcal/mol higher than for the 121 mechanism.

Clearly, the concept of a molecular mechanism for a system involving such weak bonds is oversimplified and it (like the hydrogen-bond lengths and energies estimated in this work) holds only in some statistical sense. At the same time, such a conceptual picture is extremely important in directing further simulation efforts. Most of the picture, with its necessarily complex detail, still awaits computational investigation.

Acknowledgments. I thank Jürgen Brickmann, Yasuo Kameda, and Dominik Marx for correspondence. The Fritz Haber Research Center is supported by the Minerva Gesellschaft für die Forschung, Munich, GmbH, Germany.

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