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Proton Transfer in Low Temperature Proton Conductors

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A method for the estimation of proton transfer activation energy for low temperature proton conductors based on structural data is suggested; examples of proton transfer for some specific substances are discussed.

Proton transfer is of great importance for a number of chemical and physical processes such as catalysis, sorption, energy transformation, *etc*. One of the most interesting questions in this field is the search for a correlation between proton transfer frequencies and structural factors. The problem is that proton transport essentially differs from the transport of other ions. There are some publications which deal with the proton transfer mechanisms and its dependence on different structural factors,[1–3] but a general theory does not yet exist. The main goal of this article is an attempt to elaborate a method for the preliminary estimation of the proton mobility and its activation energy based on structural data.

Possible proton transfer mechanisms. It is common knowledge that the best solid state proton conductors at low temperatures are the hydrates of acids, acid salts and some particle hydrates.[4–7] There is an opinion that proton transfer can take place either with the help of proton jumps or by means of oxonium ion transport (vehicle mechanism). There are some reasons for believing that the contribution of the vehicle mechanism to proton transfer in oxonium ions is not essential. That is why we expect that in most cases proton transfer is the sum of proton-containing group rotation and proton jumps between them.[8] Both their frequencies depend on a number of factors, the most important ones being the hydrogen bond length and the proton-accepting ability of the atoms which take part in the proton transfer. In this article we should limit ourselves to a consideration of those processes including atoms with a proton-accepting ability similar to water oxygen. This situation is the most important, because only for such compounds is defect formation easy. A number of publications exist which deal with energetic profile calculations for proton migration on the symmetric hydrogen bond; typical results are given in refs. 9–11. On the other hand, there are no correct methods for rotational potential estimation for H_nO_m groups.

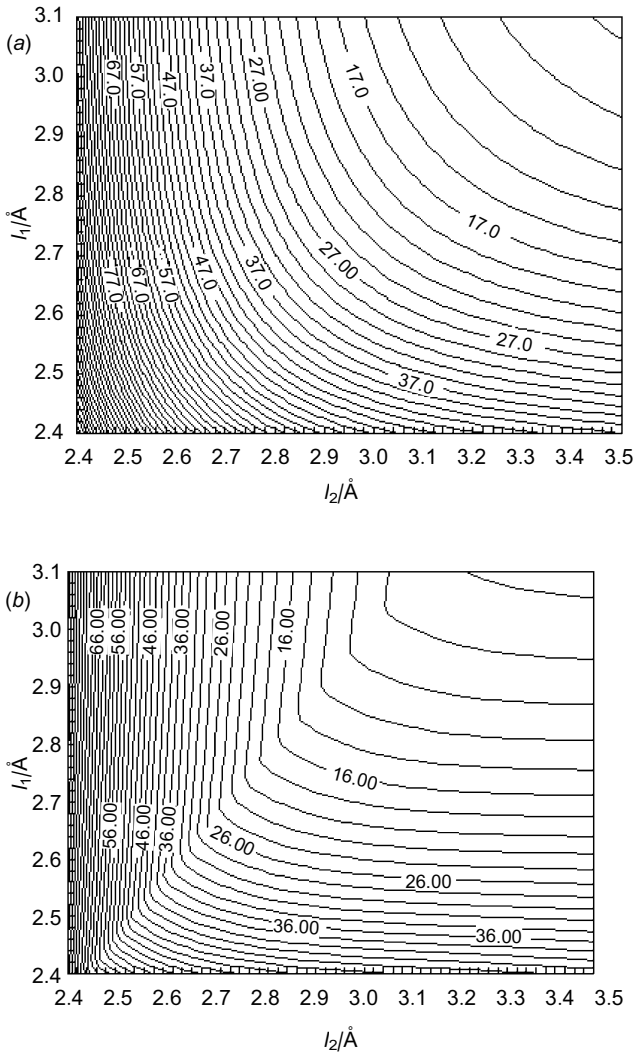

Fig. 1 The dependence of rotation activation energy (kJ mol^{-1}) on the H-bond length (l_1, l_2 and l_2) for the: (*a*) oxonium ion, (*b*) $-OH_2$ fragment of $H_5O_2^+$.

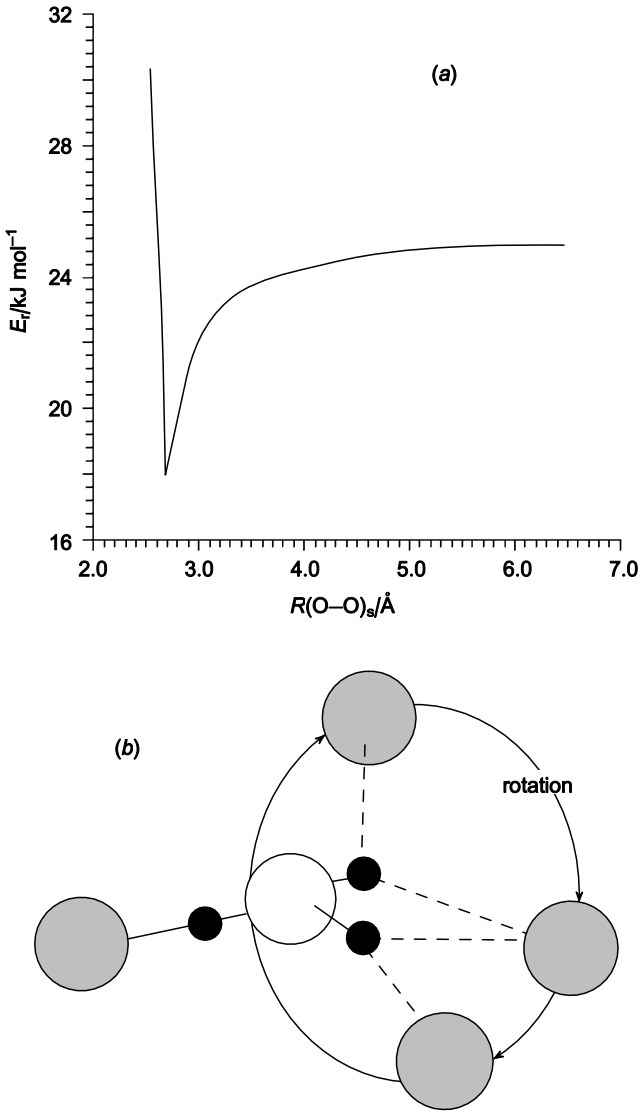

Fig. 2 (*a*) The dependence of the activation energy of X–OH_2 rotation on the R(O–O) distance. (*b*) The scheme for the activation complex with "fork" H-bonds.

Recently, we suggested a method based on the calculation of H-bond energies for different angles of rotation.[12] An example of energy surface calculation for the H_3O^+ ion rotation about a three-fold axis (H-bond lengths l_1, l_2 and l_2) is given in Fig. 1(*a*).

The role of superfluous hydrogen bond acceptors. The H_3O^+ and $H_5O_2^+$ ions cannot play the role of electron donor groups in any kind of chemical interaction (either hydrogen or M–O bond formation). On the other hand, the oxygen atoms in them are surrounded by three hydrogen atoms with typical HOH bond angles 114°.[13] In terms of close packed structures they can occupy the tetrahedral (more rarely octahedral) vacancies. This means that superfluous electronegative atom presence is typical of their environment.[8] It is possible to show that the presence of a fourth electronegative atom near the oxonium ion leads to energy gain. Electrostatic interaction calculations show that the minimum energy for this system can be reached for an electronegative atom location *ca.* 3 A apart from the oxonium oxygen. This is connected with the familiar fact that dipole–charge interactions decrease more rapidly than charge-to-charge ones. The proton-containing group rotation makes this interaction stronger. The potential minimum is very wide and the system energy decreases by only 4 kJ mol^{-1} while R(O–O) for the superfluous H-accepting atom changes from 2.9 to 3.6 A. This means that other structural interactions should play a decisive role for this distance.

The presence of superfluous proton-accepting atoms decreases the proton-containing group rotation activation energy, Fig. 2(*a*). This effect decreases from 30% for H-bond length 3.2 A to 19% for 2.6 A. Its nature concerns new H-bond formation at intermediate rotation angles. In this case the activation barrier is determined by the energy of activation complex with "fork" H-bonds, Fig. 2(*b*). Fig. 1(*b*) shows the activation energy dependence on the lengths of two main and one superfluous hydrogen bonds for the $-OH_2$ rotating fragment.

The estimation of proton transfer activation energies. As mentioned above, the process of proton transfer is usually the sum of proton-containing group rotation and proton jumps between them. If these take place with frequencies ν_r and ν_j, we obtain for the proton transfer frequency:

$$\nu_t = \nu_r \nu_j / (\nu_r + \nu_j) \quad (1)$$

The rate of the whole process is determined by the frequency of the slowest stage ($\nu_t \cong \nu_j$ for $\nu_r \gg \nu_j$ and $\nu_t \cong \nu_r$ for $\nu_j \gg \nu_r$). On the other hand, both these frequencies obey an Arrhenius law:

$$\nu = \nu_0 \exp(-E_a/RT) \quad (2)$$

The oscillation frequency (ν_0) for proton jumps along the hydrogen bond (valence oscillations) is *ca.* 10^{14} s^{-1}.[14] For the

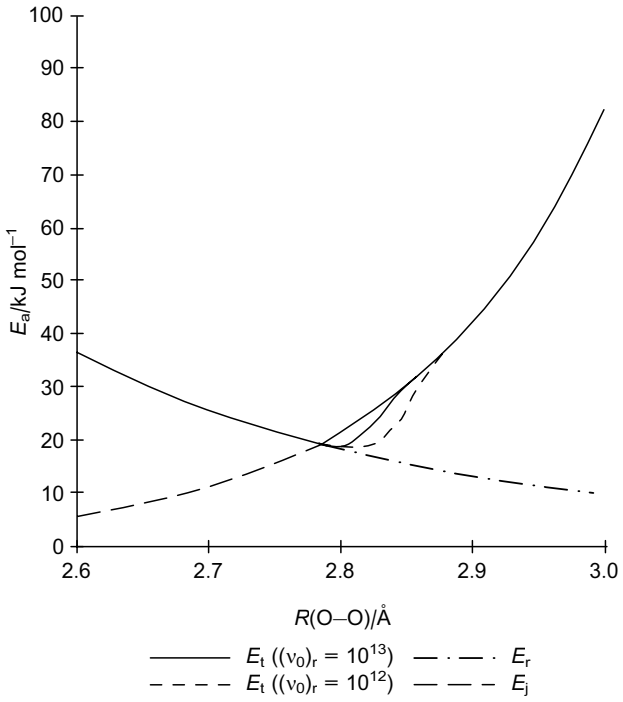

Fig. 3 Dependence of proton transfer, jumps and $-OH_2$ rotation activation energies on the hydrogen bond length for $l_1 = l_2$.

proton-containing group rotation the oscillation frequency usually has a magnitude of *ca.* 10^{12}–10^{13} s^{-1}.[14] The dependence of the frequency of both processes can be determined as:

$$\nu_j/\nu_r = [(\nu_0)_j/(\nu_0)_r] \exp[(E_r - E_j)/RT] \qquad (3)$$

An example of the calculation of the frequency and activation energies of these processes for the $-OH_2$ rotating fragment with three possible hydrogen bonds [$(\nu_0)_r = 10^{12}$ and 10^{13} s^{-1}] is given in Fig. 3. It is necessary that $(E_j - E_r) > 6$–10 kJ mol^{-1} for control of the whole transfer process by proton jumps under normal conditions.

There are two possible types of proton-containing groups: $H_xO_y^{x-2y}$ and $O_yA{-}OH^{x-}$. We believe that the activation energy for the rotation of the latter should usually be comparatively small.[8] That is why we can limit ourselves to a consideration of the activation energies for the $H_xO_y^{x-2y}$ rotation and proton jumps along the hydrogen bond. The dependence of the proton transfer process activation energy on the length of the hydrogen bond in the oxonium ion for the example of proton jumps along the two H-bonds (l_2) is given in Fig. 4(*a*). The lowest activation energy ($\cong 20$ kJ mol^{-1}) is observed for two alternative hydrogen bond lengths of *ca.* 2.8 A. The other important case is for proton transfer with the help of $-OH_2$ fragments (of H_nO_m groups) with the lowest activation energy $\cong 20$ kJ mol^{-1}, Fig. 4(*b*). It is important to note that the conductivity activation energy can be decreased by up to 16 kJ mol^{-1} for the optimum configuration with the distortion of HOH angles and some additional hydrogen bonds.

Examples of the estimation of proton transfer activation energy for some substances. In this final section we shall consider some examples of the estimation of proton transfer and proton conductivity activation energy for specific substances. The oxonium ions in thallium and indium acid sulfate monohydrates rotate at the centre of an octahedron of six anion oxygen atoms. The hydrogen bond length is *ca.* 2.87 A.[12] The corresponding activation energy of H_3O^+ rotation (E_r) is only 18 kJ mol^{-1} and is in good agreement with the NMR data.[12] The corresponding energy for the proton jumps along the hydrogen bond (E_j) is 33 kJ mol^{-1}. Proton defect formation energy can be estimated from the ^{1}H NMR data and is *ca.* 1.5 kJ mol^{-1}. The activation energy for the proton conductivity is

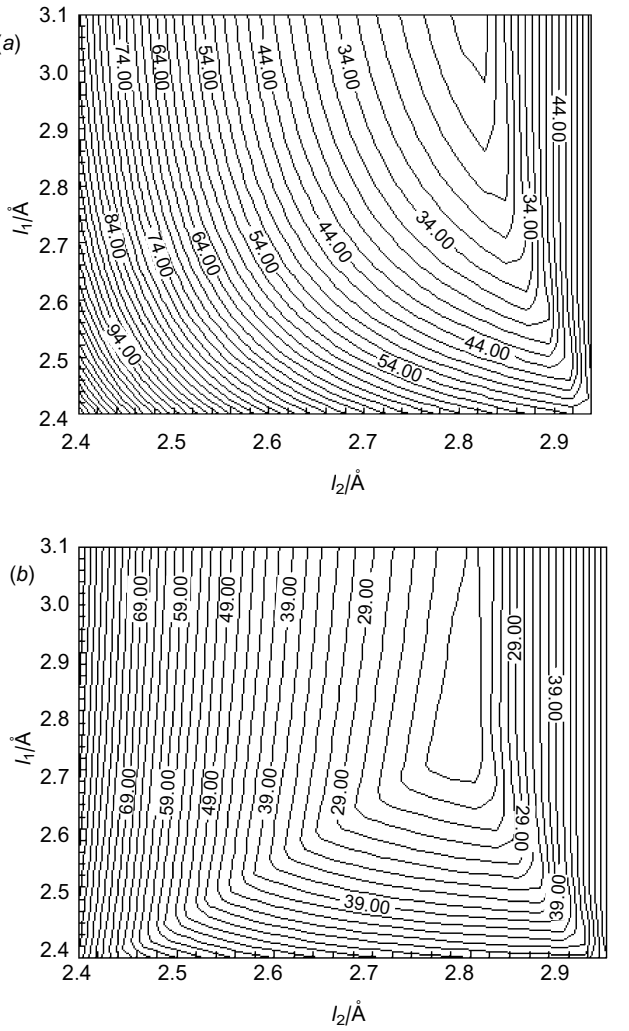

Fig. 4 The proton transfer activation energy dependence on the hydrogen bond lengths for the (*a*) oxonium ions and (*b*) $-OH_2$ fragments (see text).

$32 + 1.5/2 \cong 33$ kJ mol^{-1}. The experimental values are 30–34 kJ mol^{-1}.

It is reasonable to note that the energy of defect formation for the substances under consideration (with similar proton-accepting abilities of anion and water molecules) is usually less in comparison with the error in determination of proton migration activation energy. In most cases its contribution can be neglected as for $HUO_2PO_4{\cdot}4H_2O$. The majority of acid protons in this compound are included in the $(H_9O_4)_n^{n+}$ planes. The strongest hydrogen bond with R(O–O) = 2.56 A is a possible rotation axis. Three other hydrogen bonds have lengths 2.81–2.83 A.[15] The activation energy for the $H_5O_2^+$ ion rotation is *ca.* 18 kJ mol^{-1} and E_j is 28 kJ mol^{-1} The last is in agreement with the experimental proton conductivity activation energy, 30 kJ mol^{-1}.[5]

The external hydrogen bonds of $H_5O_2^+$ ions in $H_5O_2In(SO_4)_2{\cdot}2H_2O$ are much stronger (2.61 and 2.78 A[16]). So the maximum E_j value is 18 kJ mol^{-1} and the minimum E_r is 24 kJ mol^{-1} (this value is in good agreement with ^{1}H NMR data). The experimental proton conductivity activation energy is also 24 kJ mol^{-1}.[6] Other examples of substances whose rotational processes are decisive are the hydrates of sulfuric and nitric acids. The external hydrogen bonds of $H_{2n+1}O_n^+$ ions have lengths in the range 2.53–2.65 A[17–22] and E_r = 36–52 kJ mol^{-1}. This is why we could not find any evidence of their rotation until melting.[23]

In $H_3PW_{12}O_{40}{\cdot}29H_2O$ there are a number of hydrogen bonds of length *ca.* 2.8 A.[24] This is near the optimum for proton conductivity ($E_r \cong 17$ and $E_j \cong 22$ kJ mol^{-1}). The first

plays a decisive role, Fig. 4(*a,b*), and this is why it approaches the activation energy of proton conductivity (16 kJ mol^{-1}, ref. 4). During the cooling of this substance the situation is changing because of the inversion of the frequencies of both processes and, as a result, the activation energy is increasing.

There are a number of hydrates consisting of thin powder particles with a high surface area, so-called particle hydrates. A lot of water molecules in them are located on the surface and form ''liquid-like solutions'' of high mobility. Usually the interoxygen distances in them are in the range 2.75–2.85 A (near the liquid water ones) and they form a lattice with almost optimal configuration. These substances sometimes have very small activation energies of conductivity: up to 14–16 kJ mol^{-1} as for tin and zirconium acid phosphate hydrates.[7,25,26] These values can be higher because of the high defect formation energy for some of them.[27]

Ice has a structure close to ideal. Its low conductivity level is explained by the low defect concentration ($< 10^{-8}$ cm^{-3}). On the other hand, ice-like solid solutions doped with strong acids or bases have very high conductivity levels.[28]

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