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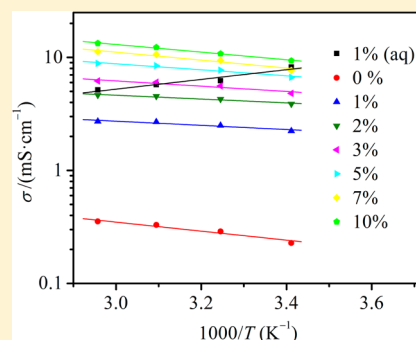
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Proton Transport Pathways in an Acid–Base Complex Consisting of a Phosphonic Acid Group and a 1,2,3-Triazolyl Group

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ABSTRACT: The proton transport pathways in an acid–base complex consisting of a phosphonic acid group and a 1,2,3-triazolyl group were studied using density functional theory (DFT) calculations in terms of stable configurations and transition states of the molecular or ionic dimers and trimers and verified by proof-of-concept experiments including experimental measurements of overall conductivity and ^1H NMR and FTIR spectroscopy of the methylphosphonic acid (MPA) and 1,2,3-triazole (Tri) complex as well as overall proton conductivity of polymeric blend of poly(vinylphosphonic acid) (PVPA) and poly(4-vinyl-1H-1,2,3-triazole) (PVTri). From the DFT calculations of dimers and trimers composed of ethylphosphonic acid (EPA), Tri, and their deprotonated counterparts, it was concluded that the intermolecular hydrogen bonds of the transition states corresponding to proton transport are much shorter than those of stable configurations, but the O–H and N–H bonds are much longer than those of stable configurations. The tautomerization activation energy decreases from 0.927–1.176 eV in Tri–Tri dimers to 0.336–0.444 eV in the EPA–Tri dimers. From the proof-of-concept experiments, about a 50 fold increase in overall conductivity was observed in the MPA–Tri complex consisting of 10% (molar ratio) MPA compared to pure Tri, and the calculated activation energy is consistent with the experimental activation energy evaluated from temperature dependence of proton conductivity of pure Tri and the MPA–Tri complex. In addition, the fast proton exchange between MPA and Tri, consistent with the DFT calculations, was verified by ^1H NMR and FTIR spectroscopy. Finally, a polymeric blend of PVPA and PVTri was prepared, and its proton conductivity at about $2.1\text{ mS}\cdot\text{cm}^{-1}$ in anhydrous state at $100\text{ }^\circ\text{C}$ was observed to be significantly higher than that of PVPA or of poly(VPA-co-1-vinyl-1,2,4-triazole). The proton conductivity of the polymeric PVPA and PVTri blend in humidity state is in the same range as that of NAFION 117.



1. INTRODUCTION

The search for alternative proton exchange membranes (PEMs) to supplement or even to substitute the membranes based on poly(perfluorosulfonic acid) (PFSA) has generated considerable research activities. One of the major purposes of such activities is to develop PEMs possessing high proton conductivity in dehydrated or even anhydrous states and at high temperatures, which is an essential characteristic for proton exchange membrane fuel cells (PEMFCs) operated at elevated temperatures.¹ At elevated temperatures, the activities of electrocatalysts are greatly improved allowing reduced loading of precious metals on the electrocatalysts,² and the tolerance of electrocatalysts to impurities in the feed-gas is also improved allowing minimized purification cost for feed-gas.³ Therefore, both manufacturing and operational costs for PEMFCs are effectively reduced.

Among the many high-temperature PEMs, polymeric acid–base complexes are competitive candidates owing to their promising conductivity in dehydrated or even anhydrous states and at temperatures as high as $180\text{ }^\circ\text{C}$. The proton transport mechanism in polymeric acid–base complexes differs from that in traditional PEMs based on PFSA and other sulfonated polymers. In the sulfonated polymers, transferable protons are generated during the hydration of sulfonic acid groups, and both vehicular and structural transport mechanisms contribute significantly to the overall proton conductivity. In the polymeric acid–base complexes in anhydrous states, only the structural

transport mechanism contributes to the overall proton conductivity.

The polymeric acid–base complexes consisting of an acidic phosphonic acid group and a basic triazole group are typical acid–base complexes for high-temperature PEMs. The triazole molecules, including various tautomeric isomers of 1H-1,2,3-triazole, 2H-1,2,3-triazole, 1H-1,2,4-triazole, and 4H-1,2,4-triazole, are promising candidates both as nonaqueous protonic solvation agents and protogenic groups. For example, the pure 1,2,3-triazole possesses an ionic conductivity of $0.130\text{ mS}\cdot\text{cm}^{-1}$ measured at room temperature with impedance spectroscopy, and pure 1,2,4-triazole possesses an ionic conductivity of $0.150\text{ mS}\cdot\text{cm}^{-1}$ at $115\text{ }^\circ\text{C}$ and $1.2\text{ mS}\cdot\text{cm}^{-1}$ at melting point of $120\text{ }^\circ\text{C}$.^{4,5} The intra- and intermolecular proton transport mechanisms have also been studied using density functional theory (DFT) calculations and other computational methods in systems based on triazole and protonated triazole.^{6–8} On the other hand, the phosphonic acid is a promising protogenic group owing to its high proton conductivity even in anhydrous states and at high temperature.^{9–11} Therefore, improved proton conductivity is expected in complex consisting of phosphonic acid group and triazole group. The ionically cross-linked poly(vinylphosphonic

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acid)—poly(1-vinyl-1,2,4-triazole) complex possesses a proton conductivity of $2.5 \mu\text{S}\cdot\text{cm}^{-1}$ at 180°C in the anhydrous state, and 8 to $22 \text{ mS}\cdot\text{cm}^{-1}$ after humidification at 100°C closing to the NAFION 117 at the same humidity level.¹² Some of the related systems for high-temperature proton exchange membranes include polymers and copolymers containing triazole groups,^{13,14} sulfonated poly(arylene ethers) containing azole groups,¹⁵ carboxylic acid functional triazole,¹⁶ phosphonic acids,¹⁷ triazole and triazole derivatives,¹⁸ and imidazole-like dimers containing imidazole, triazole, and tetrazole.^{19,20}

In this study, the proton transport pathways in an acid–base complex composed of ethylphosphonic acid (EPA) and 1,2,3-triazole (Tri) was studied based on DFT calculations in terms of optimized stable configurations and transition states of various molecular or ionic dimers and trimers. In addition, the DFT calculations were verified by proof-of-concept experiments, including experimental measurements of overall conductivity and ^1H NMR and FTIR spectroscopy of the methylphosphonic acid (MPA) and Tri complex as well as overall proton conductivity of polymeric blend of poly(vinylphosphonic acid) (PVPA) and poly(4-vinyl-1*H*-1,2,3-triazole) (PVTri).

2. METHOD

2.1. Calculation Method. The DFT calculations were applied to the study of stable configurations and transition states of molecular or ionic dimers and trimers which may exist in the EPA–Tri complex. The elementary entities involved in the EPA–Tri complex were summarized in Figure 1. Geometries of

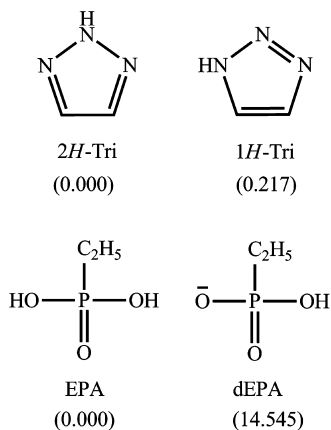


Figure 1. Molecular and ionic entities involved in the EPA–Tri complex; the values in parentheses below are energies relative to EPA or Tri in their ground states in eV.

all of the stable configurations were optimized using the B3LYP functionals with the 6-311+G(d) basis set as implemented in the Gaussian 03 package of programs.²¹ The transition states were optimized using the synchronous transit-guided quasi-Newton (STQN) method at the same level of theory as geometrical optimizations.²² If several stationary configurations were optimized with slightly different geometries, only the most stable configuration was reported. Harmonic vibrational frequency calculations were then performed to conform the optimized stable structures as minima and transitional states as saddle points. In order to simulate the impact from environment on the geometries and activation energies, the polarizable continuum model considering the molecular or ionic dimers or trimers as solute entities placed in a continuum solvent having a dielectric constant of Tri at $\epsilon = 2.61$ was applied.^{23–25} The

continuum model of Tri is reasonable to correct the geometries and activation energies as the concentration of EPA is much lower than that of Tri in this context. The B3LYP/6-311+G(d) level of theory was supposed to be suitable in such calculations and was also adopted by other researchers.^{6,8}

2.2. ^1H NMR Measurements. MPA (98%) and 1,2,3-Tri (98%) were supplied by the J&K Scientific Ltd. and Aladdin Chemistry Co., Ltd., respectively, and used as received. DMSO- d_6 (99.9%, containing 0.03% v/v TMS) was supplied by the Cambridge Isotope Laboratories, Inc. and used as solvent. The ^1H NMR measurements were performed on a Bruker AV500 MHz spectrometer with a ^1H resolution of 0.45 Hz at 295.15 K. The MPA–Tri complex solution was prepared by dissolving 40.0 mg of Tri in 0.4 mL of DMSO- d_6 first and then adding the same amount (moles) of MPA, and the mixture was sealed into a 5 × 20 mm NMR tube using TMS as reference.

2.3. FTIR Measurements. FTIR spectra were taken using an AVATAR307 Fourier transform infrared spectrometer. The MPA–Tri complex for FTIR measurement was prepared by dissolving 40.0 mg of Tri in 0.3 mL of DMSO- d_6 first and then adding the same amount (moles) of MPA. After that, the DMSO- d_6 solution of the MPA–Tri complex was spread on the KBr crystal, and the solvent and moisture were carefully removed by evaporation under an infrared lamp. Finally, the FTIR spectra were taken at 298.15 K.

2.4. Proton Conductivity Measurements. The conductivity of Tri and MPA–Tri complex was measured using a Mettler Toledo conductivity meter of model FE30. The molar ratios of MPA to Tri were 1%, 2%, 3%, 5%, 7%, and 10% in the MPA–Tri complex, respectively. The equipment was first calibrated using the standard solution ($1.416 \text{ mS}\cdot\text{cm}^{-1}$) before the actual conductivity measurements. The test tube holding 4 mL of the sample was placed in an oil bath whose temperature was controlled using a digital thermostat. The temperature was varied from 293.15 to 338.15 K, and three measurements were taken consecutively to obtain an average value at each temperature.

2.5. Preparation and Characterization of Polymeric Blend Membrane of PVPA and PVTri. The proton exchange membrane based on PVPA and PVTri blend was prepared from their mixture solution in trifluoroacetic acid (TFA). The PVPA was synthesized by free-radical polymerization of vinylphosphonic acid (VPA).²⁶ In a typical synthesis, 1 g of VPA, supplied by Tokyo Chemical Industry Corporation, Ltd. and used as received, was dissolved in 10 mL of dimethylformamide (DMF, China National Medicines Corporation, Ltd.), and 0.02 g of azobisisobutyronitrile (AIBN, Aladdin Industrial Inc.) was added as initiator. The reaction mixture was evacuated and backfilled with nitrogen three times to eliminate oxygen and water and was heated to 80°C for 24 h. During the polymerization process, white solid PVPA gradually precipitated. Finally, the reaction mixture was filtered, and a white solid was obtained and dried at 115°C for 24 h.

The *N*-protected monomer of 1-pivaloyloxymethyl-4-vinyl-1,2,3-triazole was synthesized by dipolar 1,3-cycloaddition between azidomethyl pivalate and 4-butynol and followed by dehydration.^{27,28} The *N*-protected monomer (1 g) was then polymerized in CH_2Cl_2 (10 mL, China National Medicines Corporation, Ltd.) by free-radical polymerization using AIBN (0.02 g) as initiator at 80°C for 24 h. After elimination of solvent CH_2Cl_2 by evaporation, a very viscous liquid was obtained. The viscous polymer was then dissolved in 10 mL of $1.0 \text{ mol}\cdot\text{dm}^{-3}$ NaOH solution of mixture solvent of alcohol and water ($v/v = 1/$

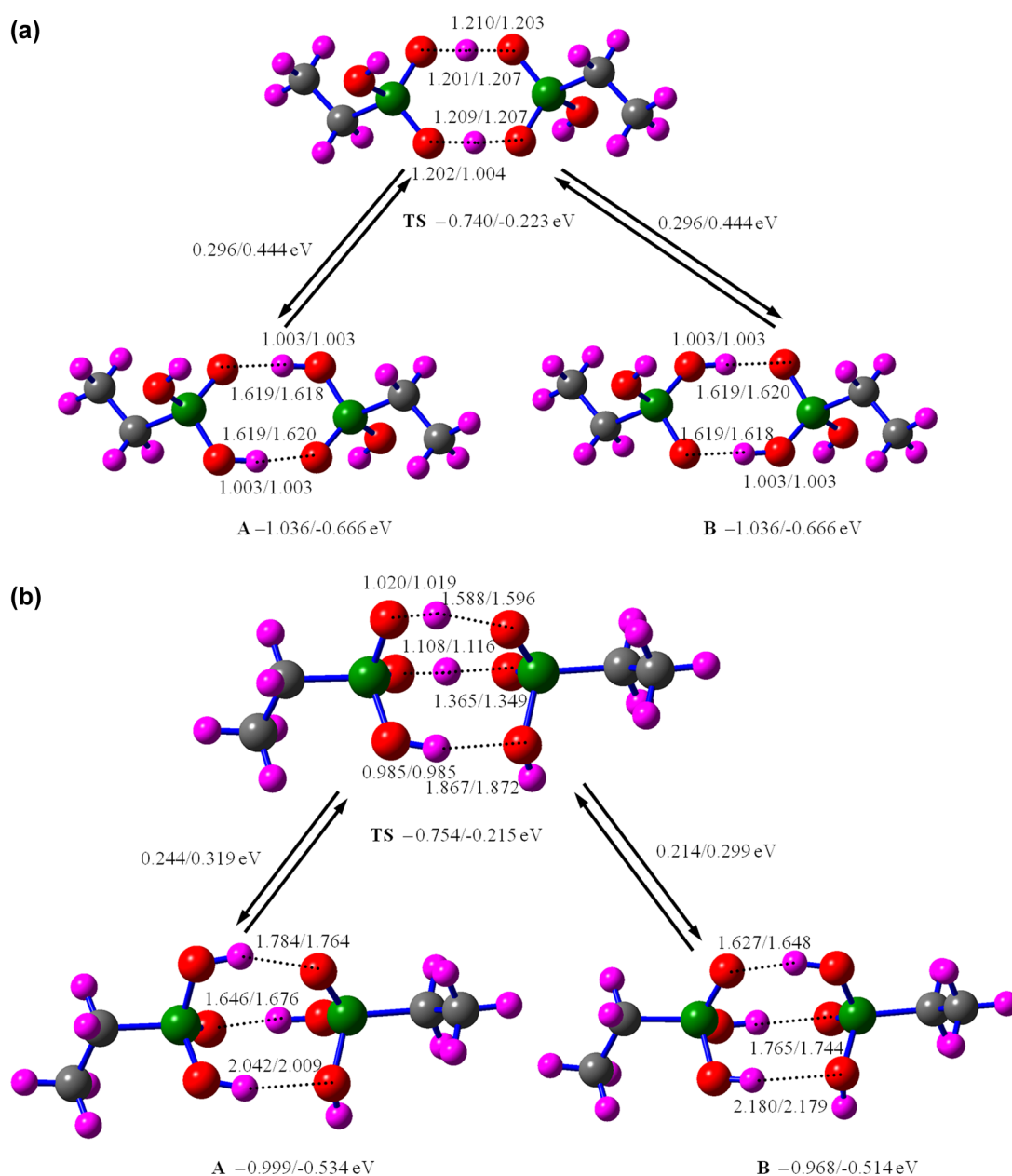


Figure 2. Proton exchange pathways between two EPA molecules, (a) with two hydrogen bonds and (b) with three hydrogen bonds. The binding energies and activation energies are shown below in eV, and corresponding geometries and energies corrected by the polarizable continuum model of Tri are shown following the slash. A and B are initial and final configurations, and TS corresponds the transition state (color code: gray for C, green for P, red for O, and purple for H).

1), and hydrolyzed for 2 h at 30 °C. After neutralization by HCl solution, yellow solid PVTri was obtained and dried at 115 °C overnight.

In order to prepare the proton exchange membrane of the PVPA–PVTri blend, the PVPA and PVTri were dissolved in TFA, respectively. The transparent solutions were then mixed under vigorous stirring, and a translucent liquid was obtained. The translucent liquid was poured into a glass sink and evaporated at 30 °C for 24 h, followed at 65 °C for 24 h. After elimination of the solvent, a yellowish transparent membrane was obtained. The proton conductivity of the membrane was evaluated from the complex impedance spectra recorded using the two-probe method at different temperatures with or without humidification. The complex impedance spectra were recorded between 0.1 Hz and 1.0 MHz using the SI1287 electrochemical

interface and the 1255B frequency response analyzer (AMETEK, Inc., U.K.).

3. RESULTS AND DISCUSSION

3.1. Proton Exchange between Two EPA Molecules.

Though there is no net proton transport during the proton exchange between two EPA molecules, this proton exchange is important for the rearrangement of the hydrogen bond network. Two proton exchange pathways between two EPA molecules, one with two and the other with three intermolecular hydrogen bonds, were identified as shown in Figure 2. In the pathway with two intermolecular hydrogen bonds (Figure 2a), the initial and final configurations are equivalent. The binding energy of two EPA molecules is -1.036 eV, the O–H bond distance is 1.003 Å, and the intermolecular hydrogen bond distance is 1.619 Å. In the

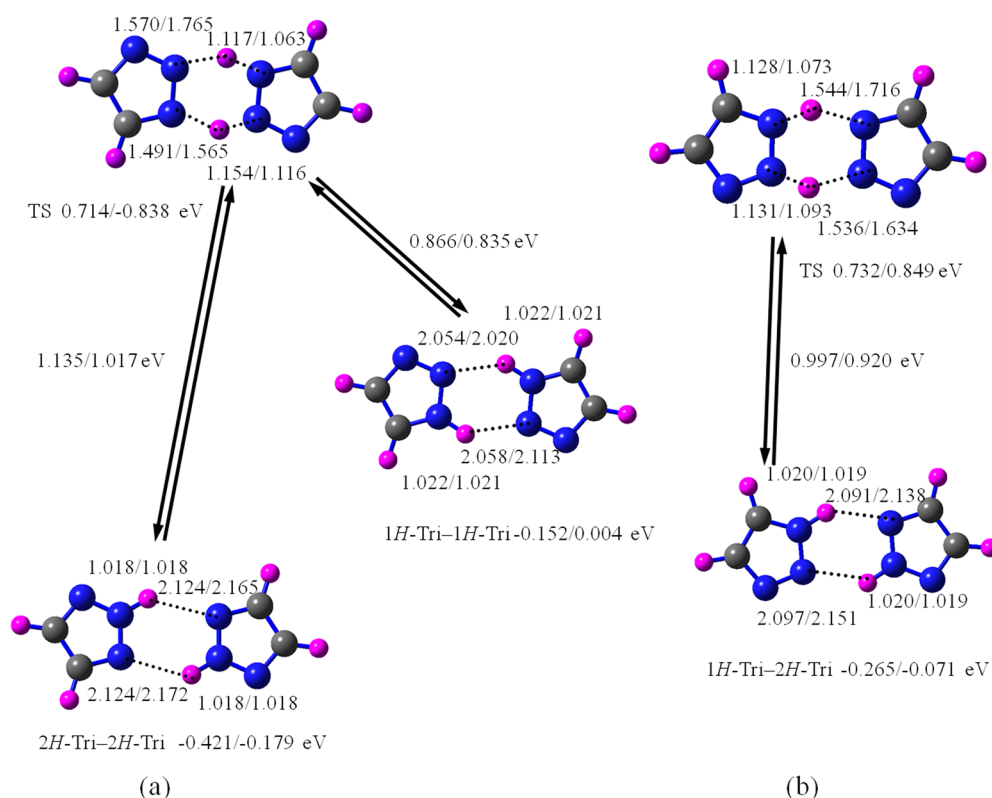


Figure 3. Tautomeric conversion between 1H-Tri and 2H-Tri, (a) with and (b) without net change in tautomeric equilibrium. The binding energies and activation energies are shown in eV, and corresponding geometries and energies corrected by the polarizable continuum model are shown following the slash (color code: gray for C, blue for N, and purple for H).

transition state, the intermolecular hydrogen bond distances are compressed to about 1.2 Å, and the O–H bond distances are stretched to similar values as the hydrogen bond distances. As a result, the equilibrium positions of the hydrogen bonded protons are adjusted almost to the middle of two EPA molecules and thus facilitating the proton exchange. The binding energy of the transition state is -0.740 eV, corresponding to an activation energy of 0.296 eV for the proton exchange.

In Figure 2b, it shows the initial and final configurations and transition state for the proton exchange pathway with three intermolecular hydrogen bonds. Despite one more hydrogen bond formed in these configurations, the binding energies for the initial and final configurations are -0.999 or -0.968 eV, slightly higher than the configuration with only two intermolecular hydrogen bonds as shown in Figure 2a. The reduction in binding energy is attributed to steric saturation of the hydrogen bonding environment. In addition, the initial and final configurations, possessing slightly different binding energies, are not equivalent to each other, and the three hydrogen bonds formed between the two EPA molecules are not equivalent, either. For configuration A, the shortest hydrogen bond has a distance of 1.646 Å, the next one of 1.784 Å, and the longest one of 2.042 Å attributed to the repulsion caused by the extra hydrogen atom bonded to the same accepting oxygen atom. For configuration B, the three hydrogen bond distances are 1.627, 1.765, and 2.180 Å, respectively. For the transition state, the hydrogen bond distances are compressed to 1.365, 1.588, and 1.876 Å, and the binding energy decreases to -0.745 eV. From these calculations, the activation energy for the proton exchange is evaluated to be about 0.25 eV, consistent with the high proton conductivity in phosphonic acid or related systems in anhydrous state and at high temperature.^{29,30} In

addition, the calculated activation energy in this work was slightly lower than the energy barrier of 7.6 kcal mol⁻¹ for the transfer of a proton in methyl phosphonic acid calculated at B3LYP/6-311G** level of theory.³¹

If a polarizable continuum model of Tri was applied in the density functional theory calculation, corresponding to cases that EPA was distributed in Tri, the activation energy for proton exchange increases about 0.148 eV of isolated EPA dimers with two hydrogen bonds; however, the activation energy does not change significantly if three hydrogen bonds were formed.

3.2. Promotion of Tautomeric Conversion of Tri via Proton Exchange with EPA. The tautomeric conversion between 1H-Tri and 2H-Tri has attracted a great number of studies, and it is concluded that the 2H-Tri is more stable in the gaseous phase but less stable in the liquid phase than the 1H-Tri.^{32–35} The tautomerization is a direct result of proton exchange between Tri tautomers and contributes to the tautomeric equilibrium as well as to the high proton conductivity of Tri. In Figure 3a, it shows the tautomeric conversion between 2H-Tri and 1H-Tri. During tautomeric conversion, two protons exchange between two tautomers, and two 2H-Tri tautomers convert to two 1H-Tri tautomers or vice versa. The binding energies for 2H-Tri–2H-Tri and 1H-Tri–1H-Tri dimers are -0.421 and -0.152 eV, respectively. Since the binding energy for transition state of tautomeric conversion is 0.714 eV, the activation energy for the conversion from two 1H-Tri to two 2H-Tri is 0.866 eV and is 1.135 eV for the reverse conversion. For the stable 2H-Tri–2H-Tri dimer, the N–H bond distance is 1.018 Å and the hydrogen bond distance is 2.124 Å. In the transition state, the N–H bond distance stretches to about 1.13 Å and the hydrogen bond distance is compressed to about 1.53 Å.

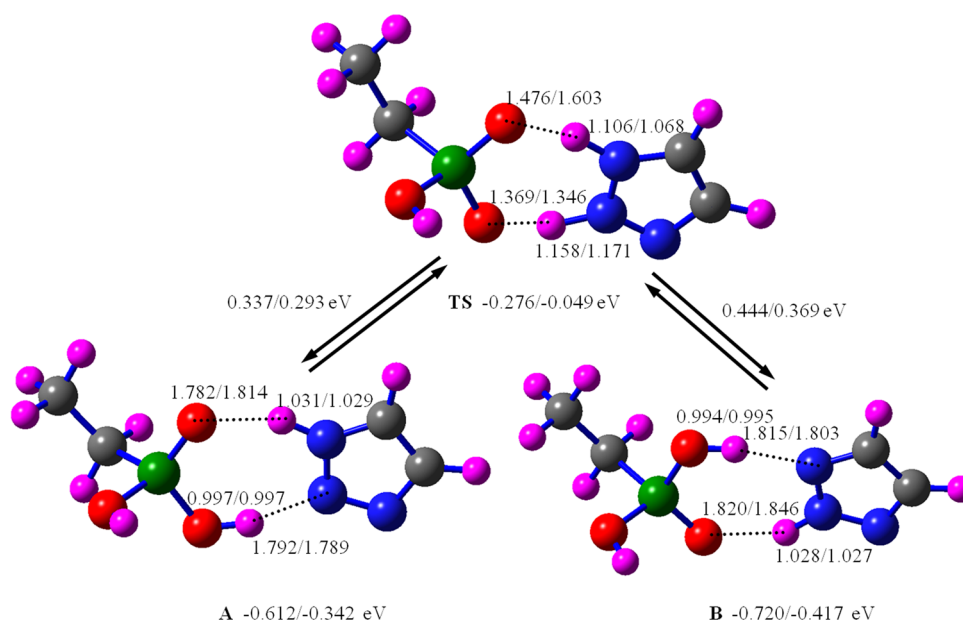


Figure 4. Promotion of tautomeric conversion of Tri via proton exchange with EPA. The binding energies and activation energies are shown in eV, and corresponding geometries and energies corrected by the polarizable continuum model are shown following the slash (color code: gray for C, green for P, red for O, blue for N, and purple for H).

The tautomeric conversion can also occur without the net change in tautomeric equilibrium as shown in Figure 3b, where a 1*H*-Tri exchanges two protons with a 2*H*-Tri resulting the 1*H*-Tri converting to 2*H*-Tri and the 2*H*-Tri to 1*H*-Tri. The N–H bond distance in 1*H*-Tri–2*H*-Tri dimer is 1.02 Å, and the intermolecular hydrogen bond distance is about 2.09 Å, whereas in the transition state, the intermolecular hydrogen bond distance is compressed to about 1.54 Å and the N–H distance stretches to 1.13 Å. The activation energy of tautomeric conversion is 0.997 eV.

The proton exchange with EPA can promote the tautomeric conversion between 1*H*-Tri and 2*H*-Tri as shown in figure 4. For the stable configurations of the EPA and Tri dimer, the intermolecular hydrogen bond distance is about 1.8 Å and the N–H or O–H bond distance is about 1.0 Å. In the transition state of the EPA–Tri dimer, both acidic protons are attracted by the Tri with N–H bond distance at 1.106 and 1.158 Å and intermolecular hydrogen bond distance at 1.369 and 1.476 Å. This characteristic is consistent with the fact that Tri is a base and EPA an acid thus Tri has a stronger proton affinity than EPA. The binding energy is –0.612 eV for the EPA–1*H*-Tri dimer, –0.720 eV for the EPA–2*H*-Tri dimer, and –0.276 eV for the transition state. Therefore, the activation energy for the tautomeric conversion from 1*H*-Tri to 2*H*-Tri is 0.336 eV, and the reverse conversion is 0.444 eV. Compared with the activation energy of tautomeric conversion in the Tri–Tri dimer at about 1 eV, significant reduction in activation energy is observed if Tri could exchange protons with EPA, and as a result, the proton transport in Tri is improved.

From Figures 3 and 4, it could be concluded that the application of a polarizable continuum model of Tri contributes significantly to the overall combination energies of the molecular dimers of EPA–Tri; however, it only insignificantly contribute to the activation energies.

3.3. Proton Transport from an EPA to an Ethylphosphonate Anion. The proton transport from EPA to an ethylphosphonate anion (or deprotonated ethylphosphonic acid, dEPA) is one of the most important proton transport pathways

in the EPA–Tri complex. Figure 5a shows the proton transport from an EPA to a dEPA, where the two stable configurations are almost equivalent. The three hydrogen bond distances in the stable configurations are at 1.612, 1.613, and 1.920 Å. In the transition state, one of the hydrogen bonds is compressed to about 1.222 Å and the O–H bond stretches to 1.222 Å. The energy for the transition state is 12.869 eV, and that for the stable configurations is 12.771 eV. Therefore, the activation energy for the proton transport is only about 0.098 eV, negligible compared with the activation energy of proton transport in the Tri–Tri dimer. In addition, the activation energy even decreases to about 0.05 eV in the EPA–EPA–dEPA ionic trimer (Figure 5b).

From these calculations, it could be concluded that the formation of ionic species in the acid–base complex is an important factor which improves proton conductivity since the activation energy for proton transport involving an ionic species is much lower than that only involving neutral species. In pristine EPA, the concentration of dEPA is very limited, despite the fact that phosphonic acid is amphoteric molecule and self-dissociates without any solvent; and thus the proton conductivity is limited. On the other hand, the addition of Tri to EPA will greatly improve the proton conductivity of EPA since Tri can abstract proton from EPA forming dEPA. From the dissociation constants (pK_a) of EPA and triazolium at 2.39 and 1.17,^{4,36} the equilibrium constant for reaction between 1*H*-Tri and EPA in aqueous solution is evaluated to be 0.06 (Figure 6). Thus, in an aqueous solution consisting of the same amount of EPA and Tri, it can be evaluated that there are about 20% of the EPA existing in ionic form as dEPA.

3.4. Proton Conductivity of the MPA–Tri Complex. In order to verify that phosphonic acid can promote the tautomeric conversion and proton transport in Tri, the overall conductivity of pure Tri as well as MPA–Tri complex was studied. As the temperature increases from 293.15 to 338.15 K, the conductivity of pure Tri increases from 0.228 to 0.354 mS·cm^{–1}. With the addition of only 1% of MPA (molar ratio of MPA to Tri, and the same unit is used in the following text), about ten times increase in overall conductivity was observed. If more MPA was added to

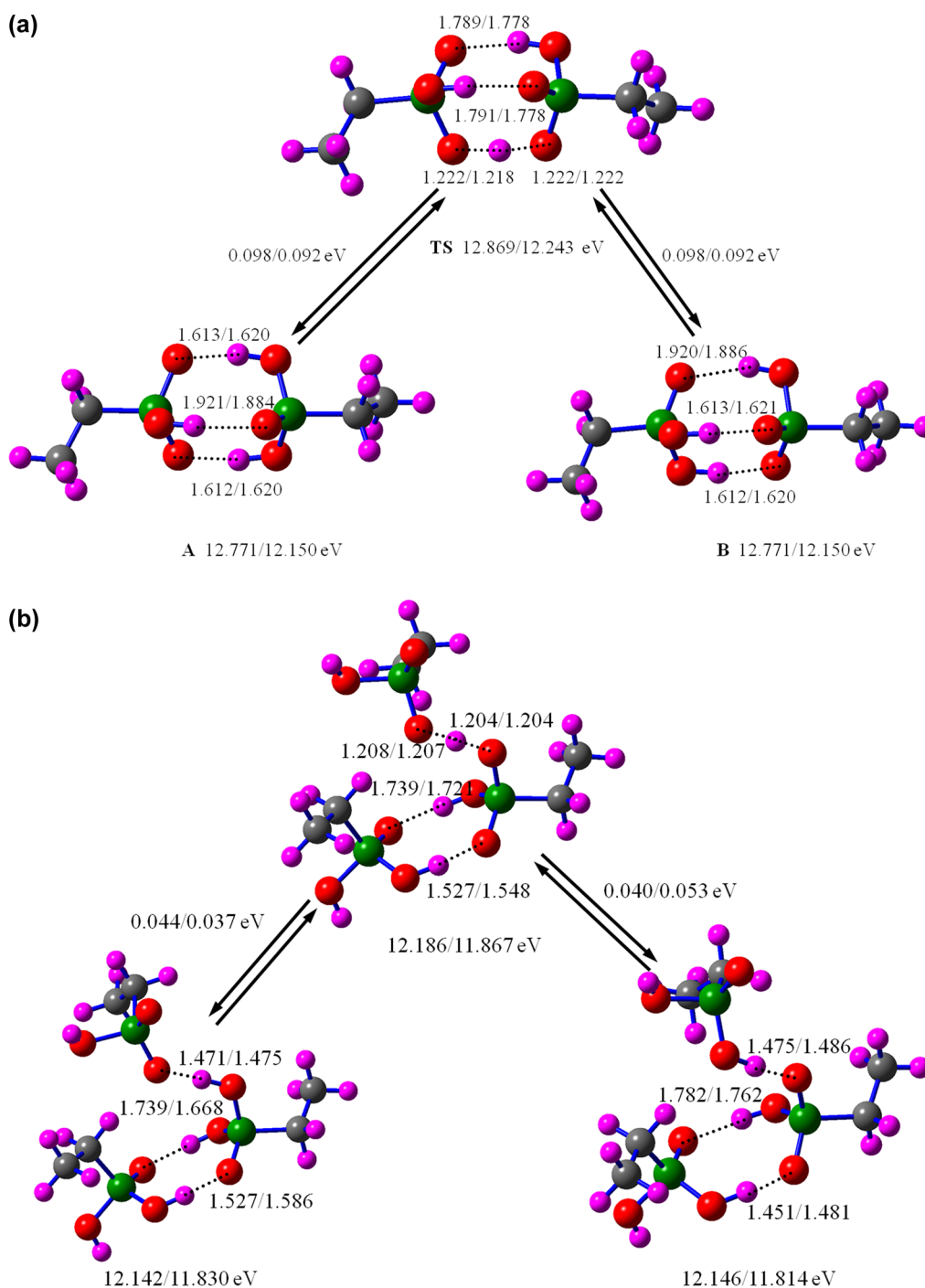


Figure 5. Proton transport in (a) EPA–dEPA ionic dimer and (b) EPA–EPA–dEPA ionic trimer. The binding energies and activation energies are shown in eV, and corresponding geometries and energies corrected by the polarizable continuum model are shown following the slash (color code: gray for C, green for P, red for O, and purple for H).

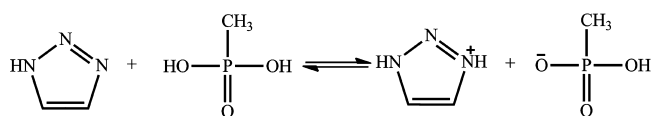


Figure 6. Reaction between EPA and 1H-Tri.

Tri, the overall conductivity increases nonlinearly with concentration of MPA (Figure 7a), and when 10% of MPA was added to Tri, the overall conductivity can increase 50 folds.

From Figure 7b, it could be concluded that the overall conductivity of pure Tri and MPA–Tri complex obeys an activation process as the logarithm of overall conductivity decreases linearly with the reciprocal of absolute temperature with correlation coefficients varying from 0.88 to 0.99 (Table 1). The activation energy for pure Tri is 0.331 eV, and this value decreases to 0.153 eV in solution consisting of 1% of MPA. If the concentration of MPA increases, the activation energy decreases to about 0.140 eV consisting of 2% MPA and then increases with the increase in MPA concentration (Table 1). In addition, the preexponential factor for conductivity increases with the increase

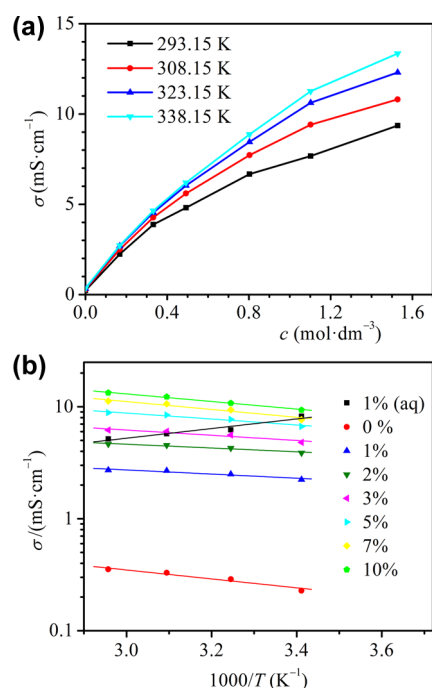


Figure 7. Proton conductivity of pure Tri and MPA-Tri complex: (a) Overall conductivity of MPA-Tri complex and (b) Arrhenius's plot of the overall conductivity of MPA-Tri complex at concentrations from 0% to 10% (molar ratio of MPA to Tri) and aqueous solution of 1% MPA (molar). The data points represent the experimental values and the lines represent the best fit to the data points.

Table 1. Activation Energy, E_a , Preexponential Factor, A , and Correlation Coefficient, r , Evaluated from Temperature Dependence of Conductivity at Various Doping Levels c (Molar Ratio of MPA to Tri)

c (%)	A (mS cm ⁻¹)	E_a (eV)	r
0	5.475	0.331	0.94
1	9.745	0.153	0.88
2	14.899	0.140	0.92
3	30.962	0.193	0.88
5	54.800	0.220	0.95
7	125.859	0.291	0.94
10	135.196	0.281	0.99
1% (aq)	0.269	-0.085	0.90

in concentration of MPA in Tri. Therefore, it was concluded that MPA promotes proton transport in Tri by reduction of activation energy, and these characteristics are consistent with the DFT calculations.

For contrast, the overall conductivity of an aqueous solution of 1% MPA (molar) was also shown in Figure 7b. However, the overall conductivity decreases with the increase in temperature, and the activation energy was evaluated to be negative at -0.085 eV. The anomalous decrease in conductivity with increase in temperature was attributed to the interruption of the hydrogen bonding network at high temperature. The MPA is a medium strong acid ($pK_a = 2.33$)³⁶ and ionized almost completely in aqueous solution. However, the deprotonated methylphosphonate anion (dMPA) is a weak acid ($pK_a = 7.67$)³⁶ and has strong electrostatic attraction with hydronium cation; thus, a strong hydrogen network forms in the aqueous solution of MPA. Therefore, the major proton transport mechanism is contributed from structural diffusion. At high temperature, the hydrogen

bond network is interrupted, and the contribution from structural diffusion of proton decreases despite the increase in contribution from vehicular mechanism. As a result, the proton transport decreases with an increase in temperature in aqueous solution of MPA.

3.5. ¹H NMR and FTIR Spectroscopy of the MPA-Tri Complex. The interaction between the phosphonic acid and Tri was also studied using ¹H NMR spectroscopy as shown in Figure 8. The assignments of spectra were based on literature values of

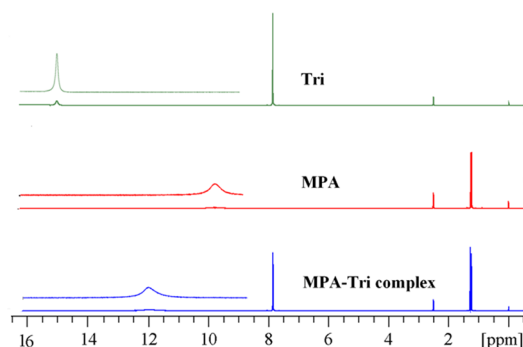


Figure 8. ¹H NMR spectroscopy of the MPA (δ 1.3 ppm for -CH₃ and 9.8 ppm for -OH), Tri (δ 7.8 ppm for -CH and 15.1 ppm for -NH), and MPA-Tri complex in DMSO-*d*₆ (δ 2.5 ppm is from DMSO-*d*₆).

MPA and Tri.^{37–39} In CDCl₃, the ¹H NMR spectrum of MPA shows two groups of proton resonances centered at 1.3 and 8.1 ppm corresponding to -CH₃ and -OH.³⁸ The ¹H NMR spectra of Tri shows two groups of proton resonances centered at 7.8 ppm (in CDCl₃ and CD₂Cl₂) and 16.9 ppm (in CD₂Cl₂) corresponding to -CH and -NH.^{37,39} In Figure 8, the chemical shifts of acidic protons of pure Tri and pure MPA are at 15.1 and 9.8 ppm, respectively. Considering the sensitivity of chemical shifts of acidic protons to solvents, DMSO-*d*₆ in our case, the peak positions and assignments were acceptable. From the ¹H NMR spectrum of the MPA-Tri complex in DMSO-*d*₆, the peak positions of the -CH₃ and -CH protons were almost unchanged; however, only one acidic proton was observed at 12.0 ppm revealing the exchange of protons between MPA and Tri.

In Figure 9, it shows the FTIR spectra of MPA, Tri, and MPA-Tri complex under anhydrous state at room temperature. We will only be interested in the frequency range corresponding to the stretching movement of acidic proton. For the MPA, the broad bands at 2336 and near 2800–2900 cm⁻¹ is due to the stretching vibration of hydrogen-bonded protons in different chemical environments.^{40,41} When MPA and Tri are blended to form a

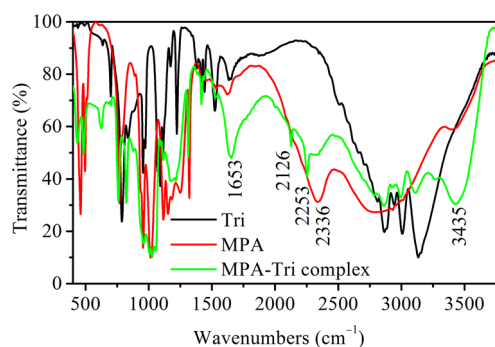


Figure 9. IR spectroscopy of the MPA, Tri, and MPA-Tri complex.

complex, sharp peaks are observed at 2253 and 2126 cm^{-1} revealing the strong intermolecular hydrogen bonding interaction in the acid–base complex. The broad signal of the MPA–Tri complex appears at 3435 corresponding to intermolecular –OH stretching.⁴² In addition, the peak at 1653 cm^{-1} , which exists in the pure MPA, pure Tri, and MPA–Tri complex, was attributed to hydrogen bonded pendent site $\text{O}(\text{N})\cdots\text{H}\cdots\text{O}(\text{N})$, and its significant increase in the MPA–Tri complex resulted from the strong hydrogen bonding between MPA and Tri.^{43,44}

3.6. Proton Conductivity of the Polymeric PVPA–PVTri Blend. Both PVPA and PVTri are highly hydrophilic and easily soluble in water; however, the polymeric blend membrane of PVPA–PVTri is insoluble in water but soluble in TFA (depending on the ratio between PVPA and PVTri). The polymeric blend composed of PVPA and PVTri (1:1 in molar ratio of the functional groups), or with less PVPA, is brittle and failed to be stripped off from the glass sink. In the ordinary dry state (being heated at 65 °C for 24 h), the polymeric blend membrane composed of PVPA and PVTri (2.7: 1) has a proton conductivity of 2.1 $\text{mS}\cdot\text{cm}^{-1}$ at 100 °C, significantly higher than the pure PVPA where a proton conductivity below 1 $\text{mS}\cdot\text{cm}^{-1}$ at 150 °C was observed⁴⁵ and the copolymer of poly(VPA-co-1-vinyl-1,2,4-triazole) with proton conductivity at about 1 $\text{mS}\cdot\text{cm}^{-1}$ at 120 °C.²⁰ In addition, the proton conductivity increase significantly as the humidity increases, and a maximum overall conductivity of 52.2 $\text{mS}\cdot\text{cm}^{-1}$ was observed at relative humidity of 100% (Figure 10). This proton conductivity is higher

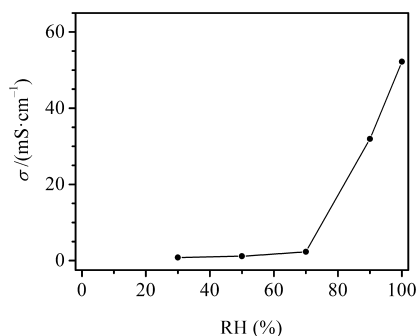


Figure 10. Proton conductivity of polymeric blend membrane of PVPA–PVTri under various relative humidity at 60 °C.

than that of cross-linked PVPA–poly(1-vinyl-1,2,4-triazole) complex ranging from 8 to 22 $\text{mS}\cdot\text{cm}^{-1}$ after humidification at 100 °C and is in the same range as that of NAFION 117 at the same humidity level.¹²

4. CONCLUSIONS

In this study, some of the important proton transport pathways, including the proton transport from EPA to dEPA and tautomeric conversion and EPA promoted tautomeric conversion between 1H-Tri and 2H-Tri, were studied in terms of stable configurations and transition states in the EPA–Tri complex. The lowest activation energy about 0.927 eV was observed for the tautomeric conversion of Tri and the phosphonic acid could promote the tautomeric conversion of Tri by lowering of the activation to about 0.336 eV. The deprotonation of EPA by Tri greatly facilitates the proton transport since the activation energy is greatly lowered when an ionic species is involved. In addition, the application of a polarizable continuum model could significantly increase the interaction between the molecular or ionic dimers or trimers,

however, the activation energies vary slightly if the polarizable continuum model is applied.

The DFT calculation results were verified by proof-of-concept experiments. About a 50 fold increase in overall conductivity was observed in Tri when 10% of MPA was added in to the pure Tri, and the experimental activation energy evaluated from temperature dependence of conductivity for pure Tri and the MPA–Tri complex is consistent with the DFT calculations. The ¹H NMR and FTIR spectroscopy of MPA–Tri complex also reveal the fast proton exchange between MPA and Tri. In addition, an overall proton conductivity at about 2.1 $\text{mS}\cdot\text{cm}^{-1}$ was observed for the polymeric PVPA and PVTri blend in anhydrous state at 100 °C, significantly higher than that for PVPA or poly(VPA-co-1-vinyl-1,2,4-triazole). And the proton conductivity of the polymeric PVPA and PVTri blend in humidity state is in the same range as that of NAFION 117.

Therefore, it is concluded that the proton transport in acid–base complexes consisting of a phosphonic acid group and a 1,2,3-triazole group is enhanced compared with their corresponding pristine systems because of the promotion of tautomeric conversion of the 1,2,3-triazole group by the phosphonic acid group, the formation of ionic species during the reaction of phosphonic acid group and 1,2,3-triazole group, and the reduction in activation energy for proton transport involving an ionic species.

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Notes

The authors declare no competing financial interest.

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