Inter*net* Electronic Journal of
Molecular Design

January 2003, Volume 2, Number 1, Pages 1–13

Editor: Ovidiu Ivanciuc

Special issue dedicated to Professor Haruo Hosoya on the occasion of the 65th birthday
Part 5

Guest Editor: Jun–ichi Aihara

Proton Transfer Reactions of R–OH·$(H_2O)_n$ (R = H_5C_2 and C_6H_5, *n* = 2, 3, 4, 6 and 12). A Computational Study

Shinichi Yamabe and Noriko Tsuchida

Department of Chemistry, Nara University of Education, Takabatake–cho, Nara 630–8528, Japan

Citation of the article:
S. Yamabe and N. Tsuchida, Proton Transfer Reactions of R–OH·$(H_2O)_n$ (R = H_5C_2 and C_6H_5, *n* = 2, 3, 4, 6 and 12). A Computational Study, *Internet Electron. J. Mol. Des.* **2003**, *2*, 1–13, http://www.biochempress.com.

Proton Transfer Reactions of R–OH·(H₂O)ₙ (R = H₅C₂ and C₆H₅, *n* = 2, 3, 4, 6 and 12). A Computational Study[#]

Shinichi Yamabe* and Noriko Tsuchida

Department of Chemistry, Nara University of Education, Takabatake–cho, Nara 630–8528, Japan

Abstract

Motivation. Hydroxyl groups in aliphatic and aromatic compounds are readily subject to proton exchanges. Aliphatic alcohols are neutral, while aromatic ones are weakly acidic. It is a question whether those well–known phenomena in aqueous media may be described uniformly in a framework of molecular interactions, *i.e.*, hydrogen bond functions. A systematic analysis of proton transfer reactions in EtOH(H₂O)ₙ and PhOH(H₂O)ₙ has been carried out.

Method. Density–functional theory calculations, B3LYP/6–31G* and B3LYP/6–311+G(2d,p), with the Onsager's SCRF solvent effect were performed for the title reactions, and proton–relay reaction paths were determined.

Results. First, the minimal and optimal model of a proton exchange reaction, Et–OH·(H₂O)ₙ→Et–OH•·(H₂O)ₙ, was sought. The *n* = 3 model was found to give a strain–free hydrogen bond network with the smallest activation energy for the concerted proton transfer. In larger models, such as Et–OH·(H₂O)₆ and Et–OH·(H₂O)₁₂, the Et–OH·(H₂O)₃ unit was confirmed to involve the concerted proton–relay movement. The transition states of proton transfers in Et–OH·(H₂O)ₙ (*n* = 6 and 12) are of the ion–pair character. Similar proton–relay reactions of Ph–OH·(H₂O)ₙ→Ph–OH•·(H₂O)ₙ were traced. A crucial difference between Et–OH·(H₂O)ₙ and Ph–OH·(H₂O)ₙ is the absence or presence of an ion–pair intermediate. That is, the ion–pair intermediates with Cs–symmetric structures were obtained in Ph–OH·(H₂O)ₙ (*n* = 6 and 12).

Conclusions. Proton–exchange reactions and absence or presence of the electrolytic dissociation were suggested to be described uniformly by the R–OH·(H₂O)₃ unit.

Keywords. Hydrogen bond; proton transfer; phenol; ethanol; transition state; ion pair; density–functional theory.

1 INTRODUCTION

Representative aliphatic and aromatic alcohol compounds (R–OHs) are ethanol (Et–OH) and phenol (Ph–OH), respectively. Et–OH and Ph–OH are dissolved in water. One unique character of their hydroxyl groups is the facile proton exchange in Eq. (1):

$$R\text{–}OD \text{ (in } H_2O) \rightarrow R\text{–}OH \tag{1}$$

The D–labeled hydroxyl group is exchanged readily in aqueous media. Although this reaction is familiar, it is strange from the standpoint of chemical–bond theory. The hydrogen bond energy is about 5 kcal/mol, while the O–H bond energy is about 90 kcal/mol. Apparently, the cleavage of the O–H covalent bond is unlikely [1]. There is a striking difference between Et–OH and Ph–OH. In water, Et–OH is neutral and Ph–OH is a weak acid (pKa = 9.95). The electrolytic dissociation in Eq. (2) occurs only for Ph–OH:

$$R-OH \rightleftarrows R-O^- + H^+ \qquad (2)$$

The acidity of phenol is usually explained by the mesomeric effect, *i.e.*, charge delocalization in the phenoxide ion [2].
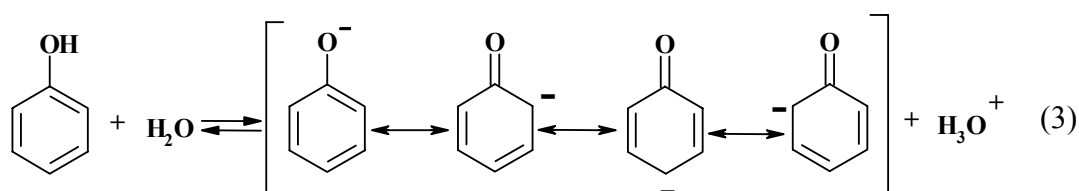
The four canonical resonance formulae in Eq. (3) give stabilization of the ion, and the proton can be released. While Eq. (3) explains the thermodynamic stability of the ion, the kinetic reactivity of the dissociation is still unresolved. Proton–transfer processes need to be elucidated for Eqs. (1) and (2). In this work, density functional theory calculations were performed to investigate reaction paths of the proton transfer. The following two questions will be answered with a computational method:

(1) What is the size of hydrogen–bond network to cause the ready proton exchange in Eq. (1)?

(2) What is the mechanistic criterion for the dissociation of hydroxyl groups in Eq. (2)?

There have been few computational studies on proton–transfer reactions of ethanol and phenol. On the other hand, there are some studies of the hydrogen bond properties. The hydrogen bond energy in EtOH···H₂O was evaluated by MP2 calculations with a frozen molecular fragment approach [3]. A proton–transfer reaction between EtOH and phenyl anion C₆H₅⁻ in the gas phase and solid was investigated. A theoretical estimate of the kinetic isotope effect due to the tunneling effect was presented [4]. The reaction between phenol and an ammonia molecule was examined. The calculated data indicated that the radical complex generated by electron ejection contains a very flat proton transfer potential connecting the excited electronic states [5]. Vibrational spectra in phenol–amine systems were reported and the OH, NH, and CH stretching fundamentals were studied [6]. The molecular dynamics simulations of the phenol hydration were carried out. Difference in free energies of hydration between molecules within a class of chemical compounds has been calculated by a coordinate coupled free energy perturbation method [7]. The equilibrium structures and energies of phenol dimers and trimers were obtained by test particle model [8]. The

acidity constant pKa of phenol was simulated by QM/MM calculations [9]. An isotope (H–D) effect on the phenol$\cdots$H$_2$O system was examined at the Hartree–Fock 4–31G and 6–31G** levels and was compared to experimental data [10]. Vibrational analyses of the phenol–(H$_2$O)$_3$ system were performed and compared with its IR spectra. Combination of theory and experiment allowed an analysis and interpretation of the experimental S$_0$ state vibrational frequencies and isotope shifts [11]. In spite of accumulation of computational and theoretical studies, the fundamental questions (1) and (2) seem not to be solved or tackled yet.

2 METHOD OF CALCULATIONS

The geometries of R–OH$\cdot$(H$_2$O)$_n$ (R = Et and Ph, n = 2, 3, 4, 6 and 12) were determined by density–functional–theory calculations. B3LYP/6–31G* and B3LYP/6–311+G(2d,p) methods [12] were used for geometry optimizations. The solvent effect was taken into account by Onsager's Self Consistent Field [13] with the dielectric constant ε = 78.39 (water). B3LYP seems to be a suitable method, because it includes the electron correlation effect to some extent and the SCRF solvent effect. MP2 calculations are slightly of higher quality than B3LYP. But MP2 requires much more computation time than B3LYP for the present systems and is not practical. The SCRF effect is indispensable to describe zwitterion species in Eqs. (2) and (3), while the MP2–SCRF combination dose not work for geometry optimizations. Transition states (TSs) were characterized by vibrational analyses, which checked whether the obtained geometries have single imaginary frequencies ($v^{\ddagger}$s). All the calculations were carried out using the GAUSSIAN 98 [14] program package installed on Compaq ES 40 at the Information Processing Center (Nara University of Education).

3 RESULTS AND DISCUSSION

3.1 Search for the Best Minimal Hydrogen Bond Network for Proton Transfers

Figure 1 shows geometries and hydrogen bond energies for R–OH$\cdot$(H$_2$O)$_n$ (R = H, Et and Ph, n = 1). Hydrogen bond distances (O$\cdots$HO) are 1.8~2.0Å. The Et–OH molecule is linked with a water molecule as a proton donor and acceptor with similar energies, –6.4 kcal/mol and –6.8 kcal/mol, respectively. On the other hand, the Ph–OH molecule is bound as a proton donor to a water molecule much more strongly than as an acceptor. This difference is a foretoken of the PhO–H dissociation. On the basis of those n = 1 geometries, formation of more hydrogen bonds will be examined hereafter.

Figure 2 exhibits a proton–transfer path in EtOH$\cdot$(H$_2$O)$_2$. The reactant geometry was constructed by the use of two isomeric EtOH$\cdot$(H$_2$O)$_1$ geometries in Figure 1. In the geometry, three hydrogen bond angles (~153°) are smaller than 180°, which indicates that the network involves ring strain. In the transition state, TS (Et, n = 2), the strain is conserved and the reaction path in Figure 2 is

thought to be unlikely. An activation energy Ea was calculated by a difference of total energies between the reactant and TS. Auxiliary water molecules are required to make strain–free hydrogen bond networks.
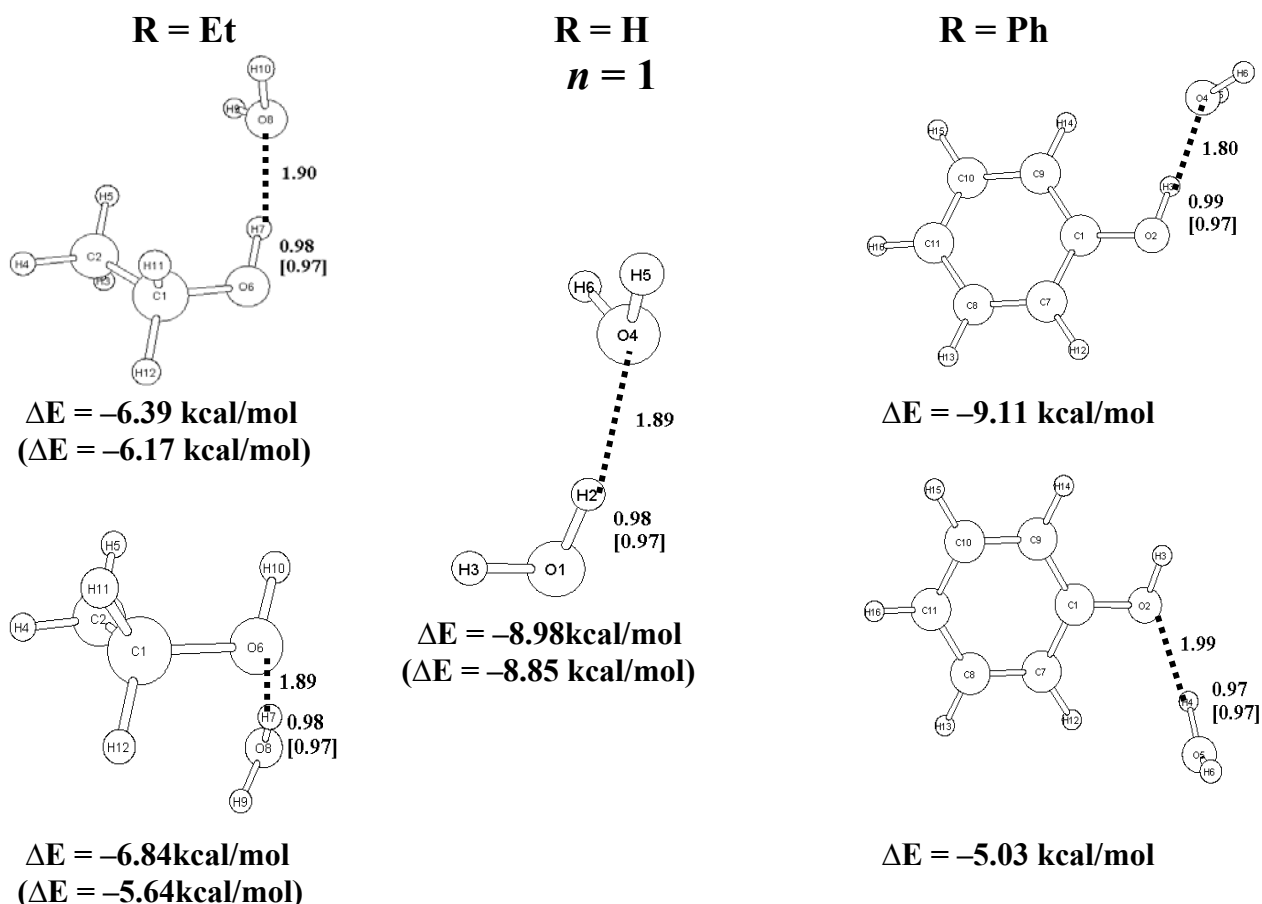
Figure 1. Isomeric geometries of hydrogen bonded systems R–OH···H₂O (R = Et, H and Ph). ΔE is the hydrogen bond stabilizing energy. Values in parentheses are the BSSE corrected energies by the counterpoise method. Distances are in Ångstroms, and those in parentheses are for free R–OH molecules (without the partner H₂O molecule for hydrogen bonding).
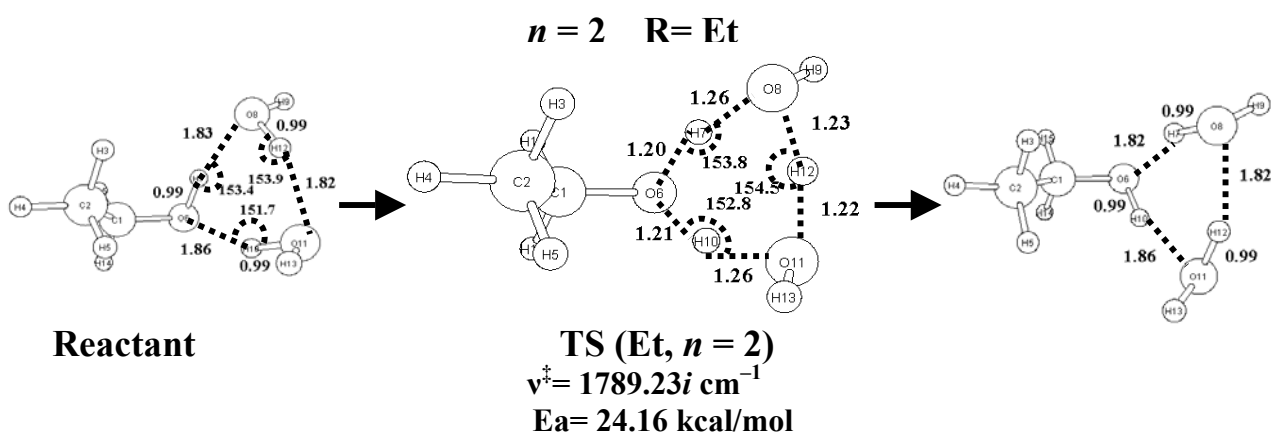
Figure 2. A proton-relay (–exchange) process in EtOH·(H₂O)₂. TS stands for transition state, and Ea is the computed energy barrier. ν‡ represents the only imaginary frequency, which verifies that the obtained geometry is at a saddle point (TS). Hydrogen bond angles are in degree.

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Figure 3 shows a reaction in EtOH·$(H_2O)_3$. In the reactant, four hydrogen bond angles are nearly 170°, and a strain–free network was attained.

$n = 3$ R= Et

Reactant   **TS (Et, $n = 3$)**

$v^{\ddagger} = 1609.56i$ $(1338.31i)$ cm^{-1}

$Ea = 20.42$ (18.81) kcal/mol

Figure 3. A proton-relay (–exchange) process in EtOH·$(H_2O)_3$. Values without and with parentheses are those by B3LYP/6-31G* SCRF and B3LYP/6-311+G(2d,p) SCRF calculations, respectively.

Along hydrogen bonds, four protons move concertedly, and TS (Et, $n = 3$) nearly with a Cs–symmetry geometry was obtained. In TS (Et, $n = 3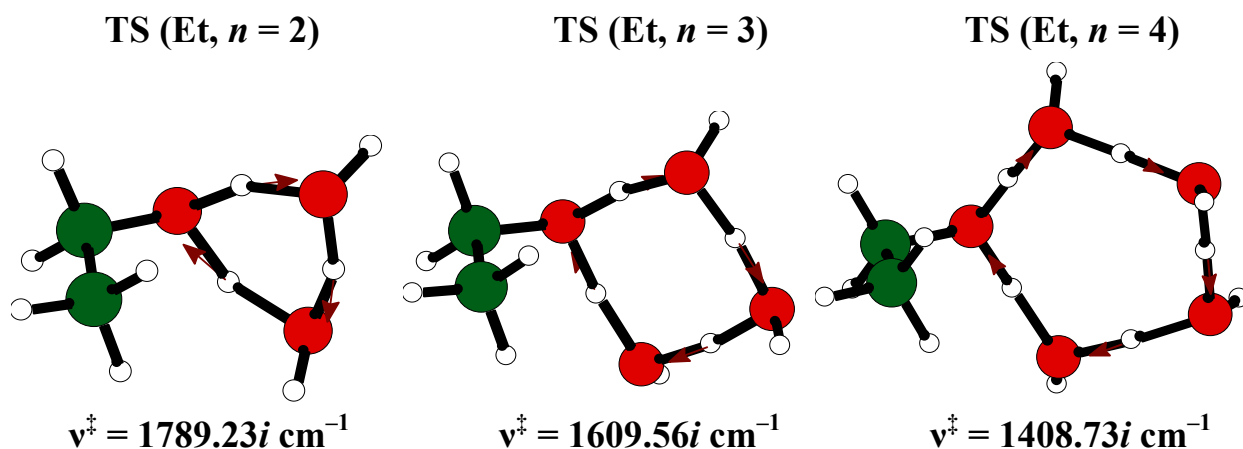$), all O···H distances are about 1.2 Å. The strain–free network gives smaller Ea value (= 20.42 kcal/mol) than Ea = 24.16 kcal/mol of $n = 2$ (Figure 2). In order to check the reliability of B3LYP/6–31G* calculations, B3LYP/6–311+G(2d,p) computations were also performed and these results are shown in parentheses. Geometries and Ea values were found to be very similar.

Table 1. Basis set dependence in B3LYP calculations of TS(Et, $n = 3$) in Figure 3. Ea is the (TS – reactant) energy difference. O6..H8 and H8..O9 are distances of one proton–relay line

Method	Imaginary frequency (cm^{-1})	Ea (kcal/mol)	O6..H8 (Å)	H8..O9 (Å)
B3LYP/6-31G(d)	1609.56i	20.42	1.183	1.249
B3LYP/6-311G(d)	1509.14i	22.63	1.131	1.308
B3LYP/6-31+G(d)	1260.96i	22.60	1.115	1.345
B3LYP/6-31G(2d,p)	1594.35i	19.66	1.179	1.242
B3LYP/6-311+G(2d,p)	1338.31i	18.81	1.123	1.316

In Table 1, basis set dependence of TS (Et, $n = 3$) was examined in more detail. While B3LYP/6–311G(d) and B3LYP/6–31+G(d) methods give somewhat larger Ea values, the dependence is acceptably small.

While EtOH·$(H_2O)_3$ was calculated to be a reasonable minimum model for Eq. (1), an $n = 4$ model must be also considered. Figure 4 shows a path in Et–OH·$(H_2O)_4$. Apparently, hydrogen bond angles of the reactant are closer to 180° than those of $n = 3$ (Figure 3).

$n = 4$ R= Et

Figure 4. A proton-relay (–exchange) process in Et-OH·(H₂O)₄.

However, the energy value, Ea = 22.63 kcal/mol, of TS (Et, n = 4) is larger than that (= 20.42) of TS (Et, n = 3). In TS (Et, n = 4), the directions of lone–pair orbitals of oxygen atoms are not fit well for the network lines. Thus, n = 3 was confirmed to be a best minimum model in Et–OH·(H₂O)$_n$ for the proton exchange in Eq. (1). Figure 5 presents the reaction–coordinate vectors of concerted proton–transfer motions in TS (Et, n). Reasonable proton movements along hydrogen bond networks are indicated by those vectors.

| TS (Et, n = 2) | TS (Et, n = 3) | TS (Et, n = 4) |

$\nu^{\ddagger} = 1789.23i$ cm^{-1} $\nu^{\ddagger} = 1609.56i$ cm^{-1} $\nu^{\ddagger} = 1408.73i$ cm^{-1}

Figure 5. Reaction-coordinate vectors corresponding to respective imaginary frequencies, $\nu^{\ddagger}$s. Geometries of TS (Et, n = 2), TS (Et, n = 3) and TS (Et, n = 4) are shown in Figures 2, 3 and 4, respectively.

Structurally and energetically, the Et–OH·(H₂O)₃ model is the best to simulate the proton exchange reaction. The highest reactivity of n = 3 is ascribed to the most favorable hydrogen bond networks both in the reactant and in TS (Et, n = 3). The good network in n = 3 is also explicable by Eq. (4):
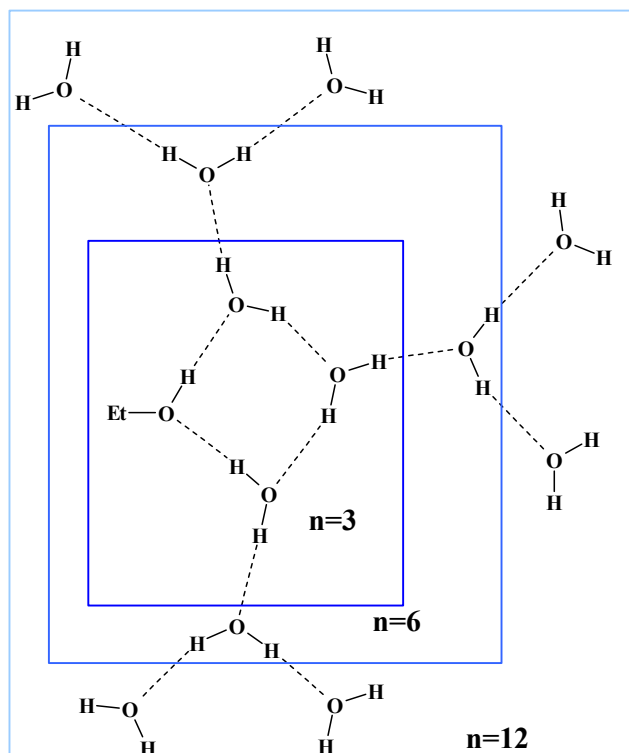
$$\text{Et–OH·(H}_2\text{O)}_{n-1} + \text{H}_2\text{O} \rightleftarrows \text{Et–OH·(H}_2\text{O)}_n \qquad (4)$$
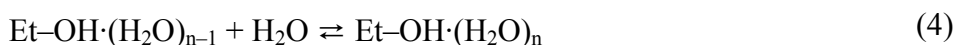
Eq. (4) describes a stepwise H₂O addition reaction. By calculating the Gibbs free energies (T = 300 K, P = 1 atm) of reactants in Figures 1–4, those changes (ΔG°s) were obtained. They are shown

in Figure 6. $\Delta G°(n = 1)$, $\Delta G°(n = 2)$ and $\Delta G°(n = 4)$ are positive values, which indicate that the Et–OH·$(H_2O)_n$ cluster ($n = 1, 2$ and 4) is less stable than the Et–OH·$(H_2O)_{n-1}$ and a free water molecule. On the contrary, $\Delta G°(n = 3)$ is a negative value, which demonstrates that only the Et–OH·$(H_2O)_3$ cluster can exist stably. Thus, the stability of the Et–OH·$(H_2O)_3$ framework has been confirmed.
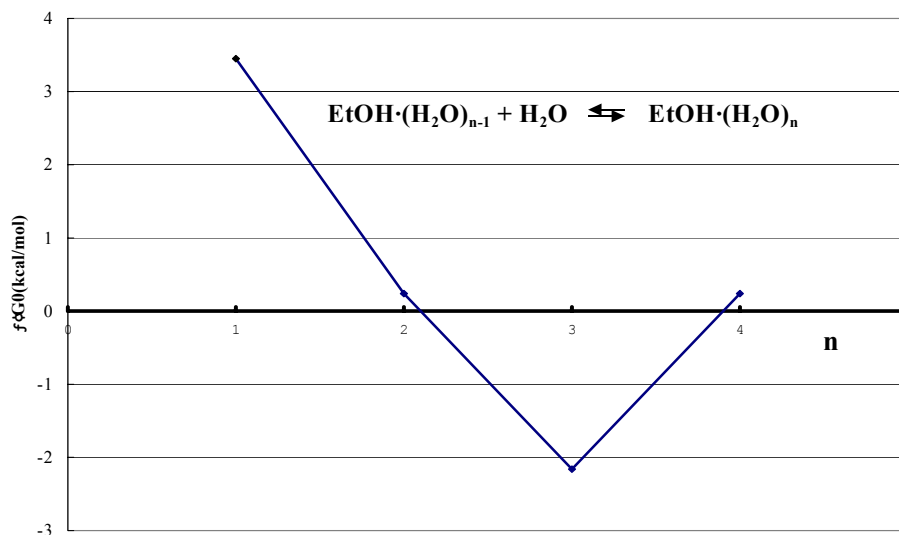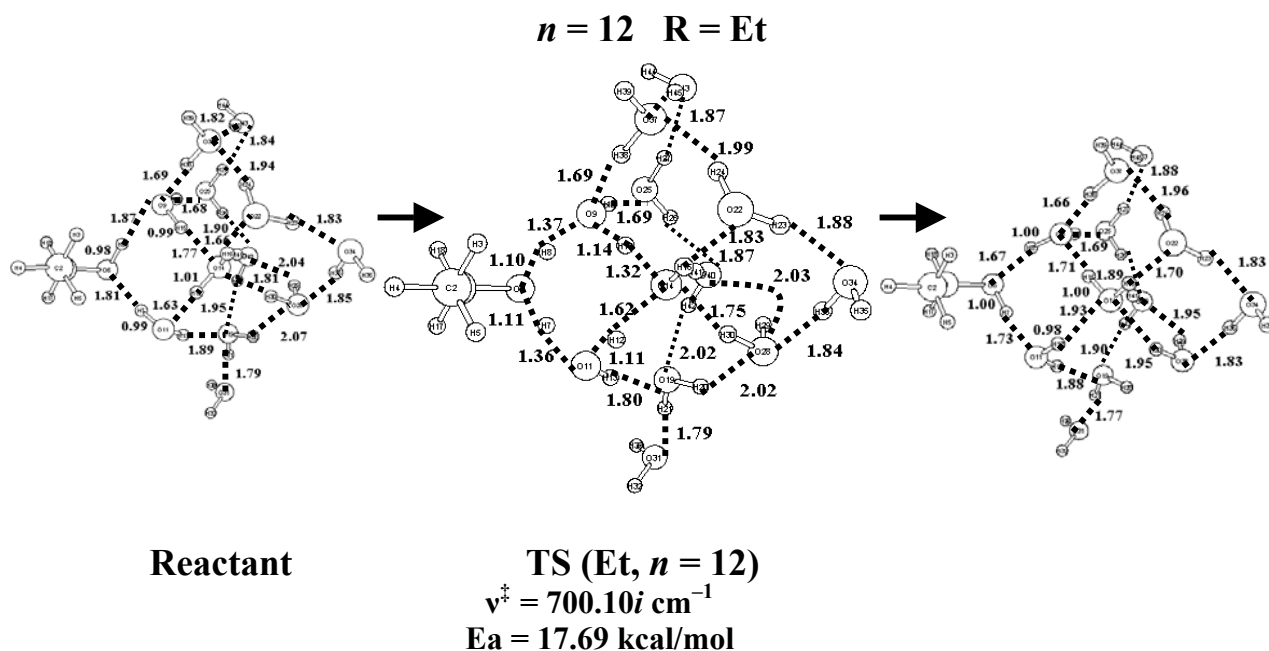

Figure 6. Changes of Gibbs free energies at T = 300 K and P = 1 atm for the stepwise addition of water molecules to the ethanol molecule.

Scheme 1. Model construction of Et–OH·$(H_2O)_n$.

3.2 Comparison of Et–OH·(H₂O)ₙ and Ph–OH·(H₂O)ₙ System

In the previous sub–section, Et–OH·(H₂O)₃ has been found to be the best model for the hydrogen bond network. Here, Et–OH·(H₂O)₆ and Et–OH·(H₂O)₁₂ will be examined on the basis of the Et–OH·(H₂O)₃ geometry (Scheme 1). Figure 7 shows a proton–relay process in Et–OH·(H₂O)₆. TS (Et, *n* = 6) is compared with TS (Et, *n* = 3) in Figure 3.

n = 6   R = Et

Reactant **TS (Et, *n* =6)**

$\nu^{\ddagger} = 680.68i\ (1113.82i)\ \text{cm}^{-1}$

Ea = 23.40 (16.81) kcal/mol

Figure 7. A proton-relay (–exchange) process in Et–OH·(H₂O)₃·(H₂O)₃.

While eight O⋯H bond distances in TS (Et, *n* = 3) are about 1.2 Å, those in TS (Et, *n* = 6) are different. TS (Et, *n* = 6) has an ion–pair like character (Scheme 2).

Scheme 2. A pseudo (not real) ion pair in TS (Et, *n* = 6).

However, there is no ion–pair intermediate, and a concerted proton relay process was confirmed in Et–OH·(H₂O)₆. Figure 8 shows a concerted process in Et–OH·(H₂O)₁₂, where a ready proton exchange in the *n* = 3 unit is recognized.

n = 12   R = Et

Reactant   **TS (Et, n = 12)**
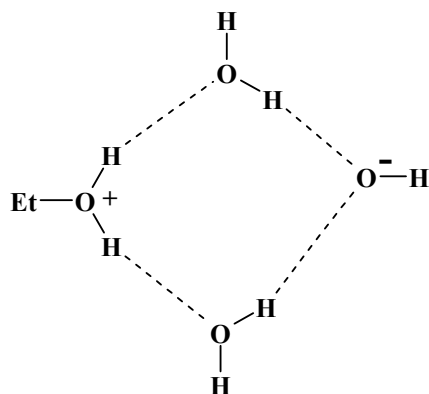$$v^{\ddagger} = 700.10i \text{ cm}^{-1}$$
$$Ea = 17.69 \text{ kcal/mol}$$

Figure 8. A proton-relay (-exchange) process in Et-OH·(H₂O)₃·(H₂O)₃·(H₂O)₆.

Noteworthy is a pseudo ion–pair character of TS (Et, *n* = 12) in Scheme 3, which is different from that of TS (Et, *n* = 6).

Scheme 3. A pseudo (not real) ion pair in TS (Et, *n* = 12).

The ion–pair character depends on number of water molecules, *i.e.*, *n* in Et–OH·(H₂O)$_n$. But, the concerted proton relay mechanism inside the Et–OH·(H₂O)₃ seems to be invariant regardless of *n*.

Figure 9 shows a proton exchange reaction in Ph–OH·(H₂O)₃. A smaller value of Ea = 17.24 kcal/mol than that of Ea = 20.42 kcal/mol of TS (Et, *n* = 3) in Figure 3 was obtained. The difference arises from that of ΔE values in Figure 1. A symmetric geometry of TS (Ph, *n* = 3) was calculated, which is similar to that of TS (Et, *n* = 3). There is no ion–pair intermediate in Ph–OH·(H₂O)₃. The Ph–OH·(H₂O)₃ model was investigated spectroscopically [11,15–17]. The stability is represented by a high reactivity of the proton transfer.
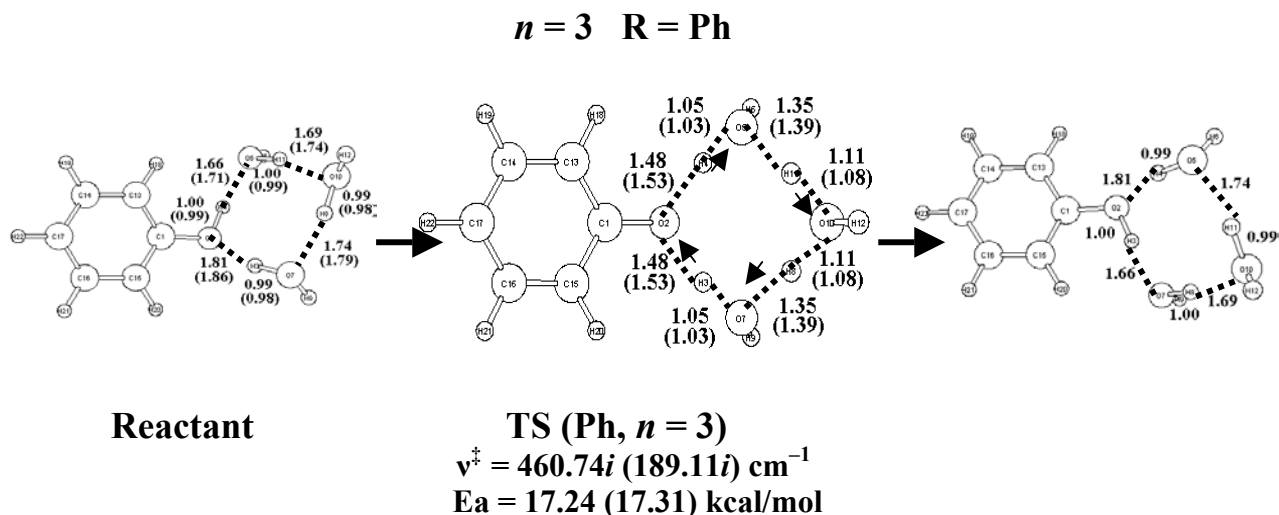
9

n = 3   R = Ph

Reactant   **TS (Ph, *n* = 3)**
v‡ = 460.74*i* (189.11*i*) cm⁻¹
Ea = 17.24 (17.31) kcal/mol

Figure 9. A proton-relay (-exchange) process in PhOH·(H₂O)₃.

Figure 10 presents a proton–relay reaction in Ph–OH·(H₂O)₆. TS (Ph, *n* = 6) has a very small Ea value (= 9.33 kcal/mol). An interesting result is that an ion–pair intermediate with a Cs–symmetry is generated after TS (Ph, *n* = 6).
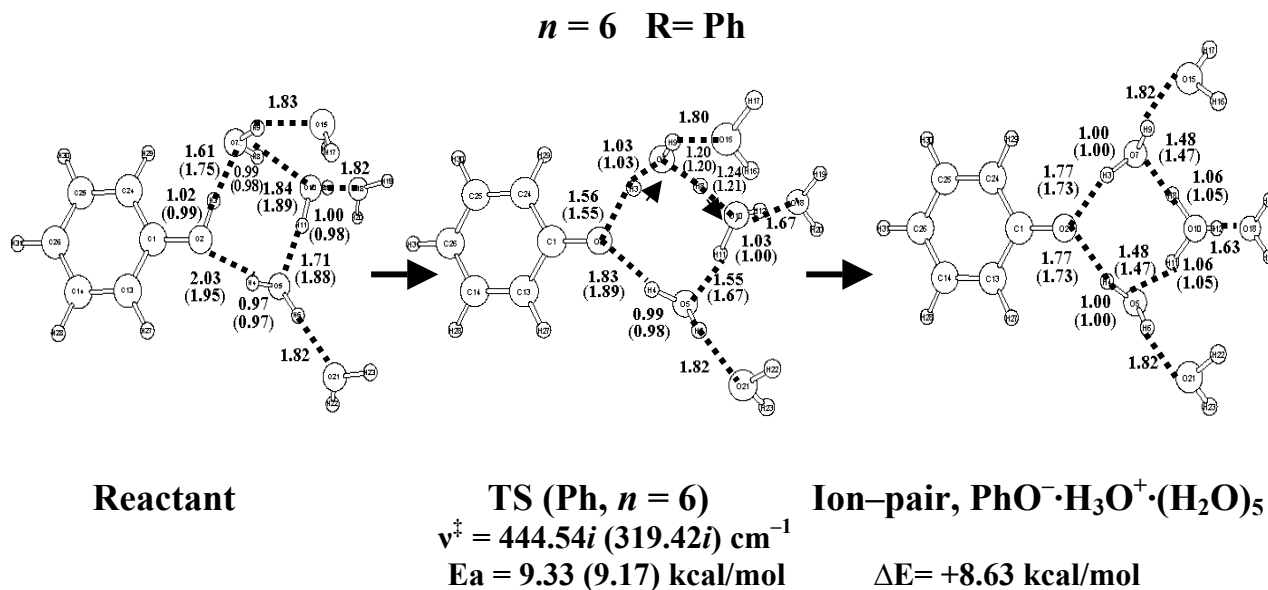
n = 6   R= Ph

Reactant   **TS (Ph, *n* = 6)**   **Ion–pair, PhO⁻·H₃O⁺·(H₂O)₅**
v‡ = 444.54*i* (319.42*i*) cm⁻¹
Ea = 9.33 (9.17) kcal/mol   ΔE= +8.63 kcal/mol

Figure 10. A proton-relay (–exchange) process in Ph–OH·(H₂O)₃·(H₂O)₃ affording an ion pair, phenoxide and hydronium ions.

Two water molecules are sandwiched by the phenoxide and hydronium ions. This chelate type intermediate exists uniquely, and the asymmetric model was not obtained (Scheme 4).
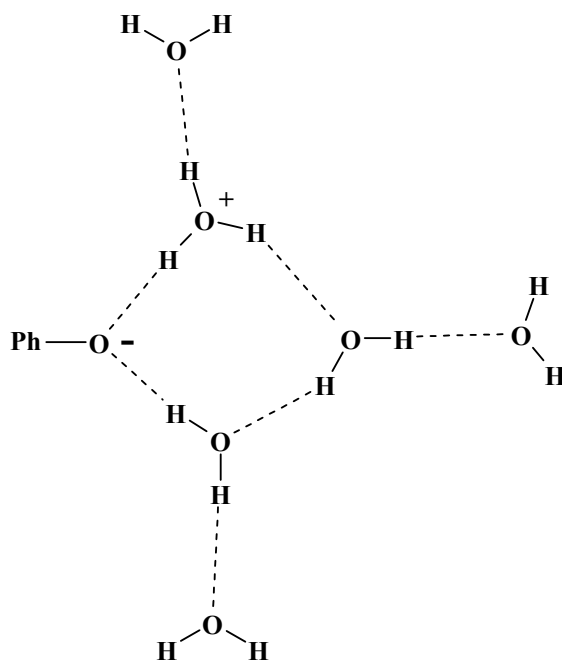
Scheme 4. Asymmetric model is absent.

To simulate the chelate type ion pair, inclusion of the SCRF solvent effect is indispensable. When we start geometry optimization without SCRF, the ion–pair geometry in Figure 10 was transformed to the reactant one.

$$n = 12 \quad R = Ph$$

Reactant

Ion–pair, PhO⁻·H₃O⁺·(H₂O)₁₁

Ion–pair, $PhO^-·H_3O^+·(H_2O)_{11}$
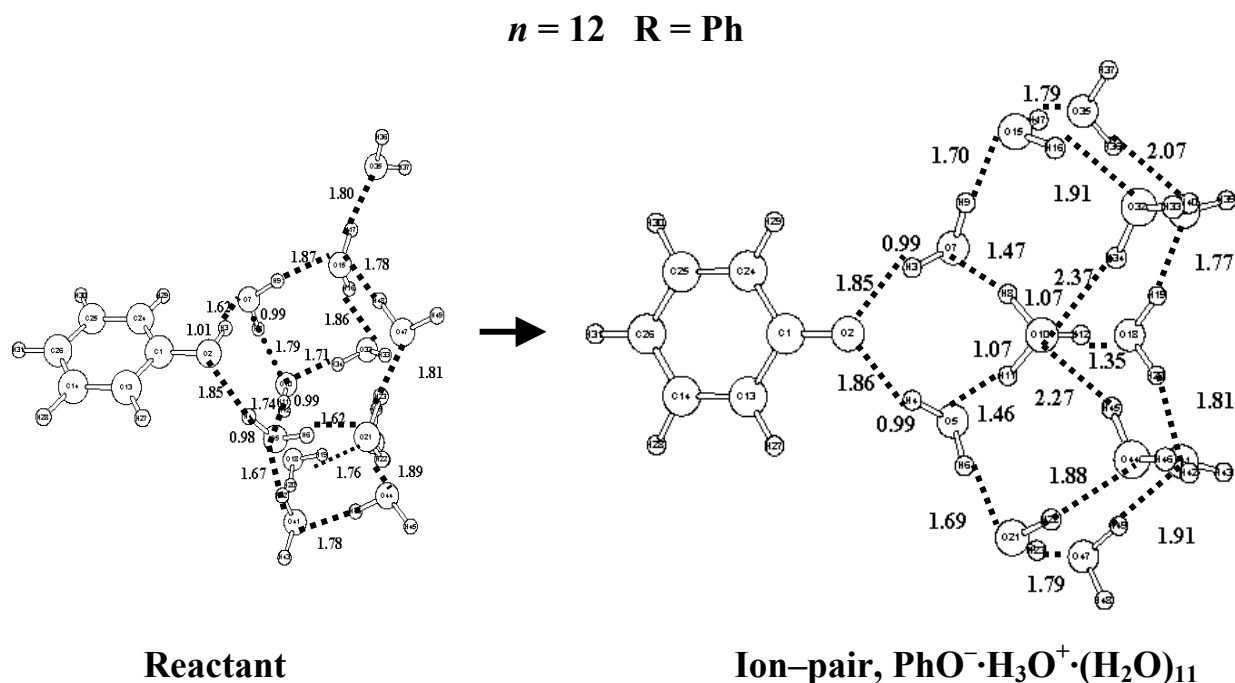
Figure 11. Geometries of the neutral precursor and the ion–pair intermediate of $Ph\text{–}OH·(H_2O)_{12}$. The TS geometry could not be obtained probably due to too many variables of internal freedom.

A decisive difference between Et–OH·(H$_2$O)$_6$ and Ph–OH·(H$_2$O)$_6$ has been found in symmetric structures. The Ph–OH·(H$_2$O)$_3$ model in Figure 9 cannot describe the ion–pair intermediate. A symmetric structure of the ion–pair intermediate was also obtained in Ph–OH·(H$_2$O)$_{12}$ (Figure 11). In the intermediate, a very short H⋯O distance is found, 1.348 Å, which indicates that proton centers may be dispersed along the outer hydrogen bond networks. That is, the acidic character may be transmitted rightward along the further hydrogen bond network.

4 CONCLUDING REMARKS

This work investigated computationally the proton transfer reactions in R–OH·(H$_2$O)$_n$. R–OH·(H$_2$O)$_3$ was found to be a minimal model to describe a proton exchange reaction in Eq. (1). Even if the model of Et–OH·(H$_2$O)$_n$ is extended to n = 6 and n = 12, the concerted reaction pattern in the Et–OH·(H$_2$O)$_3$ unit is maintained.

While TS (Et, n = 6) is of Et–O$^-$·H$_3$O$^+$ like character, TS (Et, n = 12) is of Et–OH$_2^+$·OH$^-$ one. The switch demonstrates that the proton movement is mobile along the strain–free n = 3 hydrogen bond network. For Ph–OH·(H$_2$O)$_n$ (n = 6 and 12), ion–pair intermediates with chelate structures were obtained. Thus, the electrolytic dissociation of phenol in Eq. (2) is represented by the ion–pair formation along the proton relay along the Ph–OH·(H$_2$O)$_3$ unit. Catalytic association of outer H$_2$O molecules is indispensable to describe the formation.

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Biographies

Shinichi Yamabe is professor of Chemistry at the Department of Chemistry, Nara University of Education (Japan). After obtaining the Ph.D. degree in physical chemistry from Kyoto University, Dr. Yamabe undertook postdoctoral research with professor Keiji Morokuma at the University of Rochester (USA). Recently, Dr. Yamabe has collaborated on the search for transient intermediates and mechanism of ketene–olefin reactions with professor Takahisa Machiguchi at Saitama University. Yamabe's research interest is in molecular interactions both in organic reactions and in gas–phase clusters.

Noriko Tsuchida is a graduate student pursuing her Ph.D in the Department of Chemistry, Nara University of Education under the supervision of Prof. Yamabe.