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Original research article

Can Electric Field Modulate the Formaldehyde Hydration Reactivity?

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ABSTRACT

Previous studies have shown that formaldehyde hydration $CH_2O + H_2O$, producing methanediol $CH_2(OH)_2$, can be catalyzed by the active participation of water molecules at the water droplet surface. In such cases, water molecules form a hydrogen bonding network that effectively promotes the proton relay. Considering that electric fields can exist at water interfaces, we evaluated whether an electric field can affect the water catalyzed $CH_2O....(H_2O)_2 \rightarrow CH_2(OH)_2...H_2O$ reaction. Using B3LYP/6-311+G(2d,2p), we evaluated the effect of geometry relaxation when an electric field is applied to this reaction. When a negative electric field is applied along the carbonyl carbon and water oxygen atom, the activation energy decreases, and the reaction becomes more exothermic. Furthermore, the hydrogen bonding network of the $CH_2(OH)_2...H_2O$ complex was disrupted when the field was +0.153 volts/Å. Thus, we theoretically found that the electric field can have a profound effect on disrupting important hydrogen bonding networks and can affect the reactivity.

Keywords: Density functional theory; Electric field; Nucleophilic attack; Water catalyzed reaction

1. Introduction

Water is considered the solvent of life and plays a crucial role in many biological processes due to its ability to stabilize intermediates through its polar nature and hydrogen bonding interactions, which can actively participate in reactions. Recently, water catalysis has been identified to be critical in several atmospheric reactions, including those involving Criegee intermediates, as well as in methanediol decomposition [1-3]. Several studies have highlighted the importance of the active participation of water molecules in forming hydrogen-bonded complexes, which promotes the reaction by facilitating proton re-

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lay [4-7]. Recent chamber studies have reported the competition between methanediol decomposition ($CH_2(OH)_2 \rightarrow CH_2O + H_2O$) at cloud droplet interfaces and the reaction of methanediol with OH to produce formic acid in the atmosphere [1]. On the other hand, a recent theoretical study has refuted this notion using high-level quantum chemistry calculations [8]. So there is still some confusion concerning the importance of this reaction in an atmospheric context.

One important aspect to consider is the difference between bulk aqueous conditions and water droplet interfaces. In the late 2000s, various studies have been discussing whether the air-water interface is more acidic or basic than the bulk [9-13]. We do not have a definitive answer to this question, but the studies suggest that the interface will behave differently compared to the bulk. Therefore, the droplet interface is expected to have different characteristics from the bulk. One recent theoretical study has found a slight enhancement of the electric field near the air-water interface [14]. There have been various interesting studies of electric field enhanced Diels-Alder reactions and the electric field effect on enzyme reactions [15-17]. Even a small electric field was shown to alter the reaction activation energy greatly. In such cases, Shaik and coworkers have demonstrated that the electron flow and the orientation of the electric field can be used to rationalize the catalytic and anti-catalytic effects of the electric field [16]. Considering that formaldehyde hydration involves a proton relay, we expect the electric field to modulate reactivity.

So, in this study, we aimed to evaluate the effect of the electric field on the formaldehyde hydration reaction. Considering that many previous studies have shown that water molecules may actively participate in the proton relay of this reaction, we decided to include an extra water molecule and study the $CH_2O....(H_2O)_2 \rightarrow CH_2(OH)_2...H_2O$ reaction. We focused on clarifying whether electric fields could enhance water-catalyzed methanediol production using quantum chemistry methods. We also evaluated both the static effect of modulating the energy and the active effect of modifying the water complex geometry by the electric field to gain a deeper understanding.

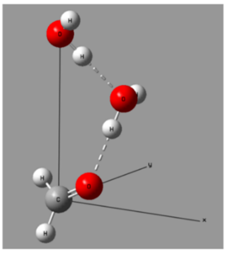
2. Materials and Methods

2.1 Energy calculation

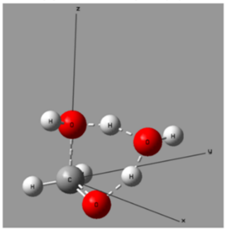
We calculated the reactant, transition state (TS), and product for the $CH_2O....(H_2O)_2 \rightarrow CH_2(OH)_2...H_2O$ reaction using density functional theory (DFT) with Becke's 3-parameter hybrid functional, B3LYP [18, 19], with Pople's 6-311+G(2d,2p) basis set [20] implemented in the Gaussian16 program [21]. To consider the surrounding water molecules, we also utilized the polarizable continuum model (PCM). We confirmed that the minima had no imaginary frequencies, while the TS had one. Furthermore, we followed the intrinsic reaction coordinate to confirm that the TS represents the reaction of interest. The schematic geometries are given in Fig. 1. These calculations will be referred to as field-free calculations.

2.2 Electric field calculation

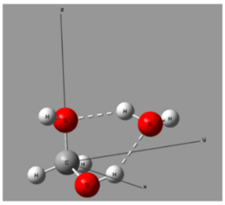
After obtaining stable geometries from the field-free calculation, we reoriented the molecule to set the formaldehyde carbon atom to be the origin. Then, the nearby oxygen atom of the water molecule was aligned to be on the Z-axis, as given in Fig. 1. We also set the carbonyl oxygen to be in the XZ plane of our Cartesian coordinate system.



(a) Formaldehyde (R)



(b) Transition state



(c) Methanediol (P)

Fig. 1. Schematic geometries of the reactant, $CH_2O....(H_2O)_2$, transition state and product, $CH_2(OH)_2...H_2O$ with XYZ axis.

The positive and negative fields were placed along the X and Z axes. A positive field indicates that we have a positive charge in the positive X or Z direction, while a negative field indicates that we have a negative charge in the positive X or Z direction. Since previous studies have reported an electric field change of 0.15 volt/$\mathring{A}$ at the water droplet surface [14], we evaluated the energies at $\vec{E}_z$= ±0.051, ±0.102, and ±0.153 volt/$\mathring{A}$, corresponding to ±0.001, ±0.002, and ±0.003 atomic units, respectively.

We performed two different calculations to evaluate the static and active effects of the electric field. For the first one, we placed the electric field on the reactant, TS, and product geometries optimized at the field-free calculation mentioned in Section 2.1. While in the second calculation, we allowed geometry optimization in the presence of the field. In all the calculations, we evaluate the forward activation energy, E_a, the backward activation energy, $E_{a,b}$, and reaction energy, E_r given by the following equations:

$$E_a = E_{TS} - E_R, \tag{2.1}$$

$$E_{a,b} = E_{TS} - E_P, \tag{2.2}$$

$$E_r = E_P - E_R, \tag{2.3}$$

where E_R, E_{TS}, E_P are the harmonic zero-point corrected energies of the reactant, transition state, and product, respectively.

Table 1. Calculated activation and reaction energies, in kcal/mol, for $CH_2(OH)_2...H_2O \rightarrow CH_2O....(H_2O)_2$ at field-free calculations.

	E_r	E_a	$E_{a,b}$
Present Work[a]	-1.38	23.2	24.6
Ref [4][b]			25.4
Ref [6][c]			27.0

a: Calculated at the PCM level,
b: Calculated at the B3LYP/6-31+G(d,p) in gas phase level.
c: Calculated at the G4 level in gas phase

3. Results and Discussion

3.1 Field free calculation results

In Table 1, we present the calculated activation and reaction energies obtained in the present study. Since previous studies reported the activation energy for the backward reaction barrier, $CH_2(OH)_2...H_2O \rightarrow CH_2O....(H_2O)_2$, we will compare our results to those calculations. We observe that our results are within a few kcal/mol of those in previous studies. Here, we note that our goal is not to calculate the absolute value of the E_a or E_r, but rather to get the variation induced by the electric field. Therefore, the current level of accuracy will be sufficient for our goal. Lastly, from Fig. 1, we confirmed that the reaction proceeds through the formation of two bonds: the C-O bond formation at the carbonyl carbon atom and the O-H bond formation at the carbonyl oxygen atom.

3.2 Static electric field effects

In this section, we evaluate the static change in energy as a function of the Z-direction electric field. As shown in Fig. 2(a), the reactant exhibits a field dependence opposite to that of the TS and product geometries. The former decreases with positive field, while the latter two increase. Since all geometries exhibit different responses to the electric field, E_a and E_r will have field dependence.

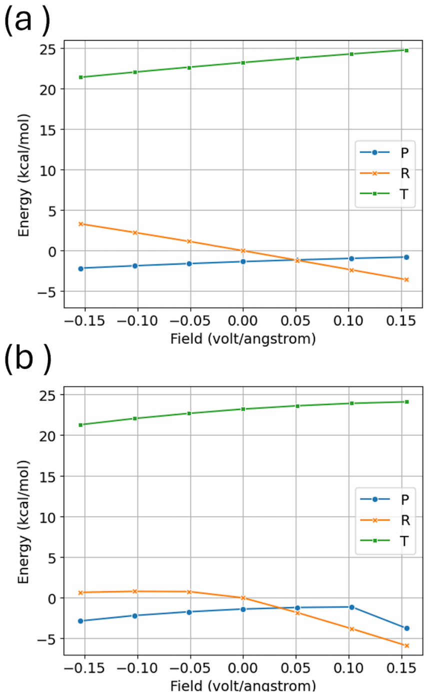


Fig. 2. Zero-point corrected energies as a function of Z-direction electric field (a) using field-free geometries and (b) using optimized geometries in the electric field. Blue, orange, and green lines stand for the product (P), reactant (R), and transition state (T), respectively.

Looking at the results given in Fig. 2(a), we can notice that the field dependence is very close to linear, and indeed we obtained a R^2 value of 0.99. However, if we fit a quadratic function of $E = E_0 + c_1\vec{E}_z + c_2\vec{E}_z^2$, we obtain a R^2 value of 0.9999. Here c_1 and c_2 are fitting parameters, but from electrostatics, the 1^{st} derivative of energy by electric field gives the dipole moment: $\frac{\partial E}{\partial \vec{E}_z} = \vec{\mu}_z$, and the 2^{nd} derivative gives the polarizability. In Table 2, we compare the fitted coefficients versus the Z-direction dipole moment calculated without the field. We can confirm that the two values are consistent, indicating that we can estimate the static electric field energy dependence from the dipole moment value in the direction of the electric field. We can see that the absolute value of c_1 can vary by 4 to 5 times at different geometries. On the other hand, the c_2 values show much smaller variation among the three geometries.

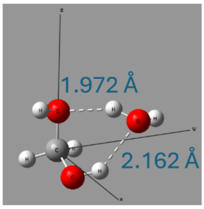
Table 2. Coefficients obtained from the fit of the electric field dependence given in Fig. 2(a), and the dipole moment in the z-direction.

Geometry	c_1 (debye)	$\vec{\mu}_z$ (debye)^a	c_2 (au)
Reactant	-4.66	-4.58	-43.50
Transition State	2.28	2.33	-48.88
Product	0.93	0.92	-43.64

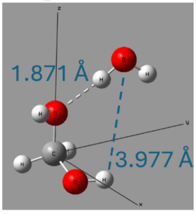
a: Results from the field-free calculation.

3.3 Geometry optimization with electric fields

In this section, we evaluate the active effect of the electric field on changing the cluster geometry and its impact on the energies. By comparing Figs. 2(a)-2(b), we observe that the electric field-dependent energies of the TS geometry (green lines) do not differ. On the other hand, the energies of the reactant (orange lines) and product (blue lines) geometries show different field dependence, especially at large fields of ±0.153 volt/$\AA$. As shown by the blue line in Fig. 2(b), the product energy as a function of electric field has a significant decrease at +0.153 volt/$\AA$. Since such a jump is not seen in Fig. 2(a), we ascribe this change in energy to the field-induced change in geometry. As given in Fig. 3, the field causes the hydrogen bonded water network in the $CH_2(OH)_2...H_2O$ complex to break. This can be confirmed from the elongation of the COH...O bond from 2.16 $\mathring{A}$ to 3.98 $\mathring{A}$ in Figs. 3(a)-3(b), respectively. Considering the upper limit of hydrogen bonding is OH...O < 3 $\mathring{A}$ [22], at +0.102 volt/$\mathring{A}$ given in Fig. 3(a), we can say there are two hydrogen bonds and the water molecule acts as both proton donors and acceptors. However, at +0.153 volts/$\mathring{A}$ given in Fig. 3(b), the water molecule only serves as a proton donor.



(a) $\vec{E}_z = 0.102$ volt/Å



(b) $\vec{E}_z = 0.153$ volt/Å

Fig. 3. Product geometry calculated at $\vec{E}_z$ =(a) +0.102 volt/$\mathring{A}$ and (b) +0.153 volt/$\mathring{A}$. The blue numbers represent the OH...O bond length in $\mathring{A}$.

3.4 Electric field dependence of activation and reaction energy

After evaluating the effect of an electric field on the reactant, TS, and product energies, we evaluate the field effect on E_a and E_r. As given in Fig. 4, the Z-direction electric field has a positive correlation with the activation energy. Therefore, we can say that a negative field will lower the E_a and thus have a catalytic effect in promoting the aldehyde hydration reaction. Examining the reaction energy presented in Fig. 5, we can also observe that a negative field will lead to a more exothermic reaction, thereby favoring the production of methanediol. Here, Fig. 5 shows an interesting trend: the positive electric field can change an exothermic reaction into an endothermic one. Not only does the reactivity change, but the thermodynamic equilibrium can also be affected by the electric field.

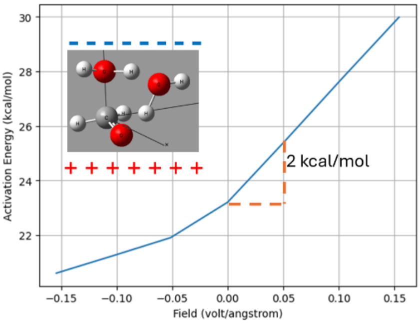


Fig. 4. Zero-point corrected activation energies as a function of Z-direction electric field for $CH_2(OH)_2...H_2O \rightarrow CH_2O....(H_2O)_2$ reaction. Schematic image of the TS under negative $\vec{E}_z$ is also given.

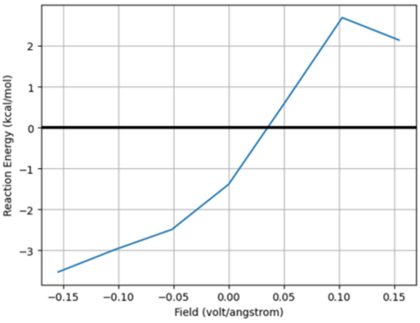


Fig. 5. Zero-point corrected reaction energies as a function of Z-direction electric field for $CH_2(OH)_2...H_2O \rightarrow CH_2O....(H_2O)_2$ reaction. We emphasize the energy of 0 for the reaction energy with a horizontal black line.

Lastly, we postulate on the catalytic

effect of the negative Z-direction electric field. As shown in Fig. 1, for the reaction to proceed, the oxygen atom of the water molecule must approach the carbonyl carbon atom of formaldehyde. For the C-O bond formation, the water oxygen will act as the nucleophile, while the carbonyl carbon is the electrophile. Therefore, the C-O bond formation requires electron transfer from the water oxygen atom to the carbonyl carbon atom. Thus, the electron flows from the positive Z direction to the negative Z direction. Therefore, a negative electric field will promote this electron transfer, while a positive field will inhibit it; see the schematics in Fig. 4. This is consistent with the previous study of Shaik and co-workers, which mentioned the importance of electron flow and electric field [15, 16]. We note here that for the O-H bond formation at the carbonyl oxygen atom, the electron motion is in the opposite direction. Thereby, we may conclude that for this reaction, the key aspect controlling the TS energy is the C-O bond formation, not the O-H bond formation.

4. Conclusion

We calculated the electric field effect for the water-catalyzed formaldehyde hydration reaction producing methanediol, $CH_2(OH)_2...H_2O \rightarrow CH_2O....(H_2O)_2$ using B3LYP/6-311+G(2d,2p) with the polarizable continuum model. In this reaction, the nucleophilic attack of the oxygen atom of the water molecule to the carbonyl carbon atom forms the C-O bond, while the proton relay along the hydrogen-bonded water network forms the O-H bond. We found that the electric field in the negative direction of the C-O bond can enhance reactivity, which is consistent with the motion of the electron transfer from the water oxygen atom to the carbonyl carbon atom. Furthermore, geometry optimization in the presence of a strong electric field can disrupt the hydrogen bonding network and affect the reactivity.

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