Sulfonation Mechanism of Polysulfone in Concentrated Sulfuric Acid for Proton Exchange Membrane Fuel Cell Applications

Yidong Hu, Liuming Yan,* and Baohua Yue*

ABSTRACT: The sulfonated polysulfone is a competitive proton-conducting material for proton exchange membrane fuel cells because of its relatively low cost and adequate performance compared with the perfluorinated sulfonic acid ionomers. This material can be economically synthesized by postsulfonation of commercial polysulfone; however, the inadequate sulfonation degree and the chain-scission degradation during sulfonation prevent the further optimization of its overall performance. In this work, the sulfonation mechanism of polysulfone is studied in terms of the transition state and activation energy based on density functional theory calculations, and the optimization of sulfonation processing parameters are discussed.

1. INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are promising technology for vehicle applications in the post-fossil-fuel world.1,2 However, the large-scale commercialization of PEMFCs is hindered by the high cost of the essential materials, including the proton exchange membranes (PEMs) and the electrocatalysts.3 Therefore, the cost reduction or the development of low-cost PEMs and electrocatalysts is of great priority for the commercialization of PEMFCs.4

The perfluorinated sulfonic acid (PFSA) ionomers, e.g., NAFION, represent the state-of-the-art materials for PEMs, owing to their outstanding performances; however, PFSA ionomers are notorious for their high cost.5,6 In order to cut down the cost of PEMs, sulfonated polysulfone (SPSF) is developed as one substituent of PFSA because of its chemical and thermal stability, excellent mechanical property of its aromatic backbone, adequate proton conductivity contributed by the high concentration of the sulfonic acid groups, and low cost.7–10 For example, Lurrano et al. synthesized SPSF from commercial polysulfone using trimethylsilyl chlorosulfonate as the sulfonation agent at room temperature and achieved a proton conductivity of 43 mS cm⁻¹ at 80 °C, glass-transition temperature between 200 and 220 °C, and power density of 400 and 500 mW cm⁻², respectively, in H₂/air and H₂/O₂ fuel cells.19,20 By optimization of the sulfonation degree, SPSF can exhibit comparable performances in a direct methanol fuel cell (DMFC) with NAFION 115.21 Furthermore, sulfonated poly(ether sulfone) (SPES),22,23 sulfonated poly(aryl ether sulfone) (SPAES),24,25 and sulfonated poly(phenyl sulfone) (SPPS)26–28 are also synthesized, which partially fulfill the PEMFC applications.

Though sulfonated polysulfone can be synthesized by postsulfonation of commercial polysulfone, the adequate sulfonation degree is difficult to achieve as the insufficient sulfonation will limit the overall proton conductivity, and oversulfonation will lead to chain-scission breakage of the polymeric backbone thus degradation of the molecular weight, the water resistance, and the chemical and mechanical performances.29–31 Therefore, it is important to study the sulfonation mechanisms to improve the overall performances of sulfonated polysulfone. Galabov et al. optimized the transition states of the sulfonation of aromatic molecules by SO₃ using high-level ab initio calculations and verified that the sulfonation is a trimolecular process consisting of one aromatic molecule and two SO₃ molecules.32,33 Morkovnik and Akopova optimized the transition states for the processes of single-stage isomerization of bimolecular π complex that associates with a H₂SO₄ molecule into corresponding associates of sulfonic acids, which indicated that the initial associates of the benzene π complex may result from the addition of bimolecular π complexes and H₂SO₄.34 Recently, Shi suggested that the trimolecular σ complex is formed directly from the rearrangement of a weak trimolecular π complex instead of the reaction of a bimolecular σ complex and SO₃.35

In this work, we will study the sulfonation mechanisms of model molecules, which emulate the typical commercialized polysulfone, using concentrated H₂SO₄ as the sulfonation agent on the basis of density functional theory (DFT) calculations. We will search for transition states of the model systems and evaluate the activation barriers, and the solvation effect will also be evaluated by application of an implicit solvation model for the calculations.

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2. RESULTS AND DISCUSSION

The sulfonation pathways may involve various possible moieties that exist in the sulfonation environment. In concentrated H₂SO₄, it is widely accepted that there exist both SO₃ and H₂SO₄, and the actual sulfonation agent may be SO₃ or H₂SO₄ or both. The trimolecular transition states being composed of arene, SO₃, and H₂SO₄ have been optimized in the literature. In the present work, we are going to optimize the transition states involving M₁ (or M₂), SO₃, and H₂SO₄ for the trimolecular mechanism.

2.1. Sulfonation Mechanism of M₁. During the sulfonation of M₁, the sulfonation agents attack at two positions of M₁@a and M₁@b via two reactions of R₁@a and R₁@b, leading to two transition states of TS₁@a and TS₁@b and two position isomeric products of P₁@a and P₁@b.

The transition state of TS₁@a is characterized by a six-membered ring (the hydrogen atoms are not counted) as shown in Figure 1a. From TS₁@a, it can be seen that the electrophile SO₃ attacks at the M₁@a carbon from one side of the arylene ring, and H₂SO₄ attacks the hydrogen atom from the other side of the arylene ring. The complexation interaction between the SO₃ and H₂SO₄ reduces the energy barrier of TS₁@a by sharing two hydrogen atoms via two hydrogen bonds. The forming C–S(SO₃) bond has a distance of 1.881 Å, close to the C–S bond in the final product P₁@a. The leaving hydrogen atom has passed the center of the C–S(H₂SO₄), and breaking the C–H bond is elongated from its initial distance of 1.07 Å to 1.328 Å.

The transition state of TS₁@b possesses similar characteristics to the TS₁@a (Figure 1b). The forming C–S(SO₃) bond has a distance of 1.957 Å, slightly longer than the corresponding distance in TS₁@a. Also, the breaking C–H bond is 1.312 Å, slightly shorter than the corresponding distance in TS₁@a. In addition, the leaving hydrogen atom reaches almost the center of the C–S(H₂SO₄). By comparison with TS₁@a and TS₁@b, it can be concluded that TS₁@b resembles the reactant more, and TS₁@a resembles the product more.

Since the sulfonation attack at M₁@b is hindered by steric repulsion from the bulky sulfonyl linkage between the two arylene rings, the activation energy for TS₁@b is much higher than TS₁@a in both the gaseous phase and solvated state by H₂SO₄. The activation energy of TS₁@a is low at 39.5 kJ mol⁻¹ in the gaseous phase and slightly reduces to 33.7 kJ mol⁻¹ under the solvated state in the sulfonation environment of H₂SO₄ (Figure 2). For contrast, the activation energy of TS₁@b is high at 117.2 kJ mol⁻¹ in the gaseous phase and reduces to 97.9 kJ mol⁻¹ under the solvated state in the sulfonation environment. An activation energy of 97.9 kJ mol⁻¹ is high enough to exclude the sulfonation at M₁@b; therefore, it is concluded that the sulfonation product is exclusively P₁@a and rarely P₁@b.

2.2. Sulfonation Mechanism of M₂. Similar to the sulfonation of M₁, there are also two potential attacking positions for the sulfonation of M₂. However, we only optimized on the transition state of TS₂@a but failed to locate the transition state of TS₂@b. This failure is attributed to the fact that the dimethyl methylene linkage is bulkier than the sulfonyl linkage and thus the more powerful steric repulsion. The powerful steric repulsion from the dimethyl methylene linkage has excluded the formation of TS₂@b and thus the formation of P₂@b. From Figure 3, it can be seen that TS₂@a is also a trimolecular transition state resembling TS₁@a. In TS₂@a, the forming C–S(SO₃) bond has a distance of 1.863 Å, close to the corresponding bond distance of TS₁@a, and the breaking C–H bond is elongated to 1.354 Å, which also resembles that of TS₁@a.

In Figure 4, it depicts the energetics of the sulfonation reaction of R₂@a. The activation energy for TS₂@a is at 49.8 kJ mol⁻¹ in the gas phase, 10.3 kJ mol⁻¹ higher than that for TS₁@a. Under the solvated state of H₂SO₄, this activation energy slightly decreases to 48.4 kJ mol⁻¹, and the difference between TS₂@a and TS₁@a increases to 14.7 kJ mol⁻¹. That is to say, the solvation effect for TS₂@a is insignificant in the transition state involving M₁ (or M₂), SO₃, and H₂SO₄.
comparison with TS1@a. This phenomenon is attributed to the difference in polarizability of the dimethyl methylene linkage and the sulfonyl linkage. The sulfonyl linkage can form a hydrogen bond with H2SO4 in the sulfonation environment; thus it greatly interacts with H2SO4. On the other hand, the dimethyl methylene linkage interacts weakly with the sulfonation medium and thus possesses an almost untouched activation energy.

The structural parameters for the transition states are summarized in Table 1 where $l_{C-S}$ is the forming bond between C and S, $l_{C-H}$ is the breaking bond between C and H, and $l_{0-H}$ is the distance between O and the leaving H. These structural parameters are consistent with each other, indicating that these transition states are concerted.

3. CONCLUSIONS

From the DFT study of the sulfonation mechanisms of model molecules, it is concluded that the sulfonation is a trimolecular process involving one substrate molecule, one SO3 and one H2SO4 in the transition state. The SO3 and H2SO4 attack simultaneously from both sides of the arylene ring of the polysulfone, forming a six-membered ring at the transition state without counting the hydrogen atoms, and the activation barrier is compensated by the hydrogen-bonding interaction between the attacking SO3 and H2SO4 molecules. The sulfonation attacks favorably at the ortho position of the ether bond linkage, rarely at the ortho position of the sulfonyl linkage, and not at the ortho position of the dimethyl methylene linkage attributing to the steric hindrance. For the two ortho positions of the ether bond linkage, the sulfonation attacks preferentially at the arylene ring with a sulfonyl linkage instead of that with a dimethyl methylene linkage.

Under the solvation of the sulfonation environment, the sulfonyl interacts more intensively with the solvation medium than the dimethyl methylene, and the activation barrier for the previous reaction is depressed more significantly than that for the latter. Therefore, it is concluded that the sulfonation attacks preferentially at the arylene ring with a sulfonyl linkage to that with a dimethyl methylene ring.

Furthermore, the sulfonation process is more complicated except for the sulfonation reaction. The detrimental side reactions, such as chain-scission breakage and/or cross-linking, are also possible at high temperatures for a long time in the sulfonation medium. These side reactions are beyond the scope of this short paper but will be covered in our future study.

4. CALCULATION METHOD

The DFT calculations are applied to the study of sulfonation mechanisms of polysulfone. All the geometries of reactants, reactant complexes, transition states, and products are optimized at a theory level of B3LYP/6-311 + G(d), and the energies are corrected at a theory level of M06-2X/6-311 + G(d) without further optimization as implemented in the Gaussian 09 package of programs. The solvation effects are evaluated using the implicit PCM model of H2SO4 with a dielectric constant of 101 and a refractive index of 1.4183 at a theory level of M06-2X/6-311 + G(d) without further optimization. Finally, internal reaction coordination (IRC) is evaluated to connect the transition states with both the reactant complexes and products.

The bisphenol A type polysulfone (BPA-PSF) is the most produced polysulfone and thus is also the most frequently sulfonated polysulfone for the preparation of SPSF. The repeat unit of BPA-PSF consists of four arylene rings, and the two arylene rings from bisphenol A are equivalent and two from bis(4-fluorophenyl) sulfone are also equivalent. The sulfonation attacks at four possible positions (1, 2, 3, or 4 position), forming four position isomers of monosulfonated BPA-PSF as depicted in Figure 5.

In the DFT study of the sulfonation mechanism of polysulfone, it is possible to use a short piece of the polymeric molecule or model molecule instead of the whole polysulfone molecule since chemical reactions are usually dependent only on near range interactions. For this reason, two model molecules, M1 and M2, are designed to emulate the BPA-PSF for the DFT study of sulfonation mechanisms (Figure 5). The model molecules consist of three arylene rings, and sulfonation attacks at the middle ring. For the model molecule M1 (or M2), the two possible sulfonation positions are labeled as M1@a (or M2@a) and M1@b (or M2@b), and the

![Figure 3. Transition state of TS2@a for the sulfonation of M2.](image)

![Figure 4. Energetics for R2@a evaluated at a theory level of M06-2X/6-311 + G(d) and the PCM solvation model of H2SO4 (inset: IRC for the transition state calculations, unit: kJ·mol⁻¹).](image)

### Table 1. Structural Parameters for the Transition States

| TS      | $l_{C-S}$ (Å) | $l_{C-H}$ (Å) | $l_{O-H}$ (Å) |
|---------|---------------|---------------|---------------|
| TS1@a   | 1.881         | 1.328         | 1.307         |
| TS1@b   | 1.957         | 1.312         | 1.322         |
| TS2@a   | 1.863         | 1.354         | 1.281         |

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corresponding sulfonation reactions, transition states, and final products are labeled as R1@α (or R2@α) and R1@β (or R2@β), TS1@α (or TS2@α) and TS1@β (or TS2@β), and P1@α (or 2@α) and P1@β (or P2@β), respectively.

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**Notes**

The authors declare no competing financial interest.

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