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Solvent effect on ternary complexes formed by oxirane and hydrofluoric acid

BOAZ G. OLIVEIRA*

Institute of Environmental Sciences and Sustainable Development (ICADS), Federal University of Bahia, 47801-100, Barreiras – BA, Brazil

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Abstract: The solvent effect on derivatives of the $C_2H_4O \cdots HF \cdots HF$ ternary complex was investigated through the PCM approach and AGOA calculations at the B3LYP/6-311++G(d,p) level of theory. Continuous analysis was useful to verify the profiles of the hydrogen bond distances in the complex, specifically the $O \cdots H$, $F \cdots H$, and $F \cdots H^{\beta}$ contacts. From the viewpoint of AGOA, the configurations of the water molecules, followed by measurement of the discrete hydration energies, were unveiled. Through single point energy calculations, the hydration energies were determined *via* the supermolecule approach, and the values were corrected by the counterpoise correction of the basis sets superposition error (BSSE). In line with this, the analysis of the molecular electrostatic potential (MEP) revealed positive and negative regions, which represent the interaction sites for the water molecules regarding the oxygen and hydrogen, respectively. In an overview, the acid-catalyzed oxirane ring-opening reaction has distinct interpretations both in vacuum and in aqueous medium depending on whether the most appropriate structure of the $C_2H_4O \cdots HF \cdots HF$ trimolecular complex is taken into consideration.

Keywords: hydrogen bonds; oxirane; hydrofluoric acid; PCM; AGOA.

INTRODUCTION

Many years ago, the solvent effect on chemical and biochemical processes was studied by many research groups worldwide.^{1,2} Even taking into account the polar or non-polar nature of the solvent/solute, the benchmark in solvation studies could be understood by the interactions of the solvent molecules surrounding the solute.³ These are specific interactions with low and high concentrations of charge density and, although there are many types of intermolecular interactions,^{4–10} they are often recognized as hydrogen bonds.¹¹ Nevertheless, it is necessary to bear in mind that the solvation process must be comprehended not

* E-mail: boazgaldino@gmail.com
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only by the H-bond strengths,^{12,13} but also by the structure or conformation of the solute.¹⁴

From the theoretical viewpoint, a description of the solvent effect can be realized through the application either of continuous or discrete methods,^{15,16} or even by means of a combination of both. The first one is formulated based on quantum chemical calculations¹⁷ that are developed into a fixed reaction field that mimics a cavity fitted to cover the solute. This is limited because the specific interactions are often poorly described, in particular H-bonds. From this threshold, discrete methods are useful once each molecule of solvent is aligned into a solvation model with a description of all specific interactions,¹⁸ which is supported by adjusted force fields instead of quantum chemical calculations. On the other hand, this procedure demands extensive processing time with high computational effort, which restricts drastically its application, mainly in compounds containing site-specific solvation.

In the past, Lynschka *et al.*¹⁹ and Wang and co-authors²⁰ discussed the influence of the solvent on the H-bond regarding either its thermodynamic functions or spectroscopy parameters through comparison between a vacuum and an aqueous environment. With absence of solvent, it is well known that the H-bond strength varies drastically in conformity with the structure of the solute. For example, it could be mentioned the $C_2H_4O \cdots HF$ complex,²¹ the bimolecular configuration of which is formed by one H-bond between the lone pair of electrons of oxygen and the hydrogen of the hydrofluoric acid. However, the trimolecular possibility must also be worthwhile of study, *i.e.*, $C_2H_4O \cdots HF \cdots HF$,²² wherein three conformations with three possible H-bonds, namely $O \cdots H$, $F \cdots H$, and $F \cdots H^\beta$, (structures **I**, **II** and **III**, respectively) were assumed the most stable structures. Among these, the last one is the result of a secondary interaction between the fluorine and axial hydrogen atoms (H^β) of the hetero-ring.

Within this scenario, the main goal of this work was not devoted to an evaluation of the influence of solvent, actually water, but the manner in which the solvent behaves upon the formation of the three structures of $C_2H_4O \cdots HF \cdots HF$. It is of fundamental importance to compare the solute-solvent interaction energies on these structures with the purpose of finding systematic tendencies, as well as verify whether the recently documented calculations performed under vacuum conditions corroborates with this.²²

COMPUTATIONAL METHODS

The first step of this theoretical study was the determination of the optimized geometries of the three structures of the $C_2H_4O \cdots HF \cdots HF$ complex, which was realized using Gaussian 03W software²³ at the B3LYP/6-311++G(d,p) level of theory. In the second step, the calculations were processed to build the solvation configurations, which were modeled through AGOA software²⁴ by means of reading the cube file generated in a single point

calculation developed previously by the Gaussian 03W program. The computations of the interaction energies or hydration energies were determined based on the supermolecule approach.²⁵ The surfaces of the molecular potential were generated by gOpenMol 3.0 visualization tools.²⁶

RESULTS AND DISCUSSIONS

The values in angstroms of the H-bond distances of the complexes **I**, **II** and **III**, both in vacuum or water medium, are gathered in Table I. In agreement with the results of Lyschka *et al.*,¹⁹ it could easily be seen that all H-bonds are shortened due the influence of the water medium simulated by the PCM approach. By comparing the variations of the H-bond lengths, the O...H values are much more reduced than those of F...H, *e.g.*, the values of 0.1854 and 0.1725 are longer than 0.161 and 0.1239 of the **II** and **III** complexes, respectively. Moreover, the larger reductions in the O...H lengths also reflect on secondary interactions.

TABLE 1. Values of the H-bond distances (Å) obtained at the B3LYP/6-311++G(d,p) level of theory in vacuum and aqueous medium simulated through the PCM protocol; values of ΔR s were computed as follows: R (vacuum) – R (PCM/water)

H-bonds and medium	Structures		
	I	II	III
$R_{O...H}$ (vacuum)	1.7137 ^a (1.7144) ^b	1.5513	1.5372
$R_{O...H}$ (PCM/water)	1.5817 ^a (1.5824) ^b	1.3659	1.3647
$\Delta R_{O...H}$	-0.132 ^a (0.132) ^b	-0.1854	-0.1725
$R_{F...H}$ (vacuum)	–	1.7035	1.6706
$R_{F...H}$ (PCM/water)	–	1.5425	1.5467
* $\Delta R_{F...H}$	–	-0.1610	-0.1239
$R_{F...H^\beta}$ (vacuum)	3.1600	–	2.7550
$R_{F...H^\beta}$ (PCM/water)	3.3900	–	4.6308
$\Delta R_{F...H^\beta}$	0.2300	–	1.8758

It was demonstrated that **III** is the only structure able to form the secondary interactions between the fluorine and axial hydrogen atoms (F...H ^{β}).²² This can be clearly seen by the H-bond length of 2.7550 Å, which even longer than the sum of the van der Waals atomic radii for fluorine and hydrogen (2.67 Å).²⁷ Regardless that this distance is outside the range of the intermolecular interaction profile, (F...H) ^{β} was recognized as a typical H-bond interaction. In aqueous medium, PCM calculations revealed that (F...H) ^{β} is drastically enhanced by 1.8758 Å. In other words, secondary interactions do not influence the structures of complexes **I–III** in the aqueous medium, whereas the primary H-bonds O...H are sensitive to the influence of the solvent, which means that O protonation is the main route to the ring-opening reaction. Meanwhile, it is fundamental to know in which manner the water molecules act in these complexes, which could maybe be an explanation of the influence of the solvent in this type of reaction.

The clusters for the three structures **I–III** of the trimolecular $C_2H_4O \cdots HF \cdots HF$ complex are illustrated in the Figs S-1–S-3 of the Supplementary material to this paper. In these Figures, it can also be observed the punctual charges derived from the ChelpG protocol (Charges from Electrostatic Potentials using a Grid based method),²⁸ within the formalism of which is a picture of the electrostatic potential (*ESP*) fields, either negative (MEP_{min}) or positive (MEP_{max}), which are illustrated in Fig. S-4 of the Supplementary material. It can be seen that the water molecules are orientated towards the hydrogen atoms of oxirane as well as the fluorine atoms of hydrofluoric acid. These molecular sites possess MEP_{max} and MEP_{min} with positive values (hydrogen ChelpG charges of 0.129, 0.133, 0.120, and 0.124 eu) and negative ones (fluorine ChelpG charges of -0.420 , -0.422 , -0.438 , -0.473 , -0.481 , and -0.496 eu) respectively, and due to this, the interactions and solvation occur on the oxygen atoms and hydrogen atoms, respectively.

The ChelpG charges of -0.420 and -0.422 eu in **I** indicate that the fluorine atoms (F^a and F^b) are equally solvated by water molecules. On the contrary, the fluorines in **II** and **III** are specific solvation sites. Note that the hydrogen atoms of the water molecules surround preferably the F^b atoms, as is observed especially in **II**. About the clusters in **III**, both F^a and F^b are solvated, although the first slightly by only four water molecules. However, the shapes of these clusters corroborate with two distinct circumstances regarding the chemistry of the three-membered rings. In one of them, the solvation on F^b is in line with the open ring reaction with acid (see Fig. 1), although in the present case with two

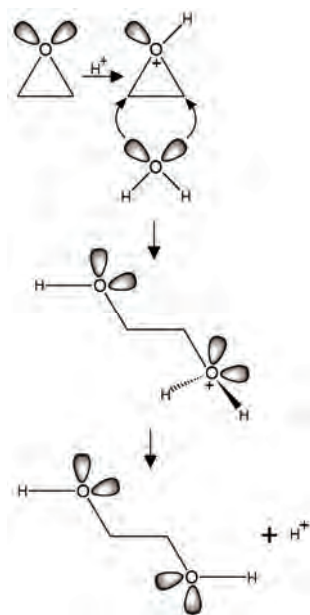


Fig. 1. Ring-opening reaction of oxirane *via* nucleophilic attack.

molecules of hydrofluoric acid, which represents an acid-catalyzed ring-opening reaction (see Fig. 2). Otherwise, the nucleophilic attack of the water molecules on the axial hydrogen atoms indicates that a S_N2 mechanism is delineated. Which of these two profile rules the oxirane open ring reaction was also one of the main goals of this work but if is not reliable, maybe in future could be.

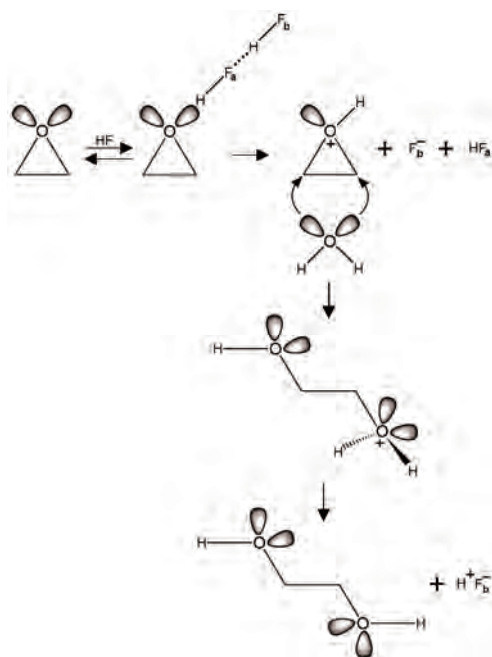


Fig. 2. Acid-catalyzed ring-opening reaction of oxirane.

A graph with all values of the hydration energies is designed in Fig. 3. The profiles of the strengths of the H-bond in **I**, **II**, and **III** are quite different. For this reason, the computation of the hydration energies by means of Eq. (1) is not a general rule:

$$E^{HYDRA} = E(\text{hydrated } C_2H_4O \cdots HF \cdots HF) - E(H_2O + C_2H_4O \cdots HF \cdots HF) \quad (1)$$

As such, ideally each hydration energy should be appraised by the H-bond energies along the $C_2H_4O \cdots HF \cdots HF$ complex, *e.g.*, $O \cdots H$, $F \cdots H$, and $F \cdots H^a$ in **III**, for instance. As the individual measurement of the H-bond energies is unapproachable,²⁹ it is not allowed in parts to use them to correct the hydration energies. In accordance with the different H-bond distances given in Table I, the complexes **I–III** are certainly formed through an unusual cooperative effect, *i.e.*, an electronic organization derived from the energy distribution among several intermolecular interactions along the supramolecular structure. However, the computations of the H-bond energies of $O \cdots F$ and $F \cdots H$ were made based on the supermolecule approach as follows:

$$CE = E_{O...H} + E_{F...H} \quad (2)$$

$$E_{O...H} = E(C_2H_4O) - 2E(HF) \text{ and } E_{F...H} = E(C_2H_4O \cdots HF) - E(HF) \quad (3)$$

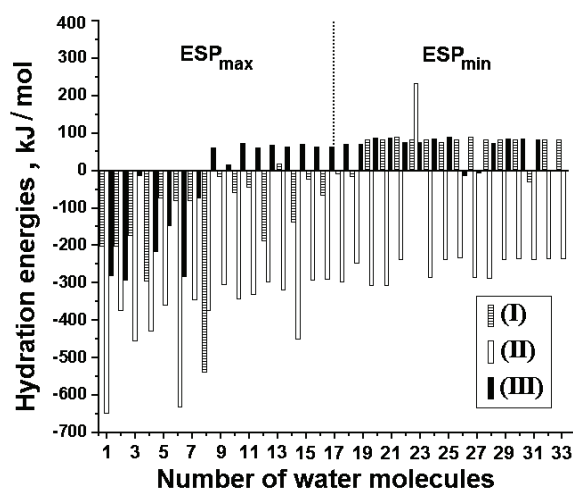


Fig. 3. Acid hydration energies of the three structures (I, II and III) of the $C_2H_4O \cdots HF \cdots HF$ complex.

In practice, the hydration energies could be used to predict accurately the most stable complex as well as which molecular site is the most sensitive to nucleophilic or electrophilic attack. Only to mention, these hydration values were not corrected by BSSE calculations because the counterpoise amounts are often very small. Through *MEP* analysis and after completing the calculations, the AGOA method suggests that the number of water molecules necessary for hydration of complexes I, II, and III are 32, 34 and 30, respectively. Regarding Fig. 3, it can be seen that I and III are the less stable structures. On the contrary, the hydration energies of II are much more stable, although there is one configuration located at a positive *MEP* or *MEP*_{max} that indicates a repulsion. This is to some extent surprising because III is the most stable structure in vacuum. On the other hand, the solvation of the water molecules on the hydrofluoric acid in II is the more appropriate to describe (see Fig. 2) a feasible mechanism for the acid-catalyzed ring-opening reaction of oxirane.

CONCLUSIONS

The acid-catalyzed ring-opening reaction of oxirane was once again studied. In this work, a theoretical survey based on PCM³⁰ and AGOA³¹⁻³⁴ calculations was presented. The influence of water as solvent was examined in terms of the H-bond properties,^{62,63} in particular the distances that were reduced upon the formation of the $C_2H_4O \cdots HF \cdots HF$ complex. In line with this, it was revealed

that the structure of this complex rules the specific configurations of the water molecules, and it was not necessary that such a structure was the most stable in the absence of solvent. Based on these evaluations, the acid-catalyzed ring-opening reaction of epoxy was described with shorter H-bond distances for protonation of oxirane, as well as solvation of the water molecules on the second hydrofluoric acid molecule.

SUPPLEMENTARY MATERIAL

Hydration clusters and *MEP* surfaces of the complexes **I**, **II** and **III** are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

УТИЦАЈ РАСТВАРАЧА НА ТЕРНАРНЕ КОМПЛЕКСЕ ЕПОКСИДА И ФЛУОРОВОДОНИЧНЕ КИСЕЛИНЕ

BOAZ G. OLIVEIRA

Institute of Environmental Sciences and Sustainable Development, Federal University of Bahia, Barreiras, Brazil

Испитиван је утицај растварача на тернарне комплексе $C_2H_4O \cdots HF \cdots HF$, применом РСМ поступка и рачунањем AGOA методом на V3LYP/6-311++G(d,p) нивоу теорије. Тиме су проверени профили водоничних веза у комплексу, посебно $O \cdots H$, $F \cdots H$ и $F \cdots H^{\beta}$ контакт. Мерењем дискретне хидратационе енергије, праћени су положаји молекула воде. Анализом електростатичких потенцијала (*MEP*) утврђене су позитивне и негативне области, које одговарају интеракцији са молекулима воде преко кисеоника, односно водоника. На тај начин је интерпретирано киселином-катализовано отварање оксиранског прстена како у вакуму, тако и у воденом раствору.

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