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Ab initio Computations for the Ring–Opening Potential of Propylene Oxide: Roles of a Proton and a Water Molecule

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Ab initio Computations for the Ring–Opening Potential of Propylene Oxide: Roles of a Proton and a Water Molecule [#]

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Abstract

Ab initio computations for the ring–opening potential of propylene oxide were carried out. The MP2/6–31G**, MP2/6–31++G**, MP3/6–31G**, MP3/6–31++G**, and QCISD/6–31G** calculations were used to obtain the most stable structure of propylene oxide. MP2/6–31G** calculations were performed for the C–O bond stretching of propylene oxide in five systems: an isolated propylene oxide, a hydrated propylene oxide, a protonated propylene oxide, a protonated and hydrated propylene oxide, and a propylene oxide with a hydronium ion. The aim of these calculations was to reveal what conditions allow spontaneous completion of the ring–opening process of propylene oxide to create a propanal. Two conclusions can be drawn from our results. The first is that the ring–opening process never proceeds spontaneously under the conditions considered in this study. The second conclusion, drawn from the IRC calculations, is that both the ring–opening process and the hydrogen transfer process occur in a one–step reaction and that the reaction paths are slightly affected by the level of basis set and electronic correlation used in the calculation. The results of the localized molecular orbitals calculations reveal that the low valence of the carbon atom of a breaking C–O bond hinders the C–O bond breaking.

Keywords. *Ab initio* computation; ring–opening reaction; propylene oxide; localized MO; IRC.

1 INTRODUCTION

The carcinogenic and/or mutagenic properties of vinyl compounds and of aromatic compounds have been investigated by many researchers. In particular, the chlorinated compounds have become well–known as strong carcinogens [1–12]. Henschler and Neudecker [1] investigated variations in the mutagenic properties of chloropropenes with respect to the number of substituted chlorine atoms and to the substituted positions. In their experiments, they used three enzyme inhibitors to trace the activated metabolic intermediates in the metabolic processes and found two metabolic pathways. One is the epoxidative pathway, in which an oxide is produced as an essential intermediate. Another

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is the hydrolytic–oxidative pathway, in which an aldehyde is produced as an essential intermediate. Although oxides are usually converted to diols by hydrolysis, Henschler and Neudecker concluded from their results that chloropropene oxides are converted to chloropropanals and not diols. In this case, oxides must be converted to propanals *via* both a ring–opening reaction and a hydrogen transfer reaction.

The ring–opening reactions of ethylene oxide and propylene oxide have been investigated by both experimental and quantum chemical computational methods [13–19]. Based on the results of thermal gas–phase decomposition and of single–pulse shock tube, it has been reported that an activation energy of 58.5 kcal/mol is needed for the ring–opening reaction of propylene oxide [13,14]. In an acidic solution, the activation energy decreases to 18.62 kcal/mol [15]. For protonated ethylene oxide, the energy is 20 kcal/mol [16]. In computational research, similar results have been obtained [17–19]. As shown in Chart 1, the oxide–to–aldehyde conversion process must include both a ring–opening reaction and a hydrogen transfer reaction. The computed results for propylene oxide indicated that both reactions proceed in concert [17]. On the other hand, it was shown that for a protonated propylene oxide, the conversion to an aldehyde does not proceed in a concerted fashion [18]. Duuren has described the carcinogenic action of vinyl chloride [20], indicating that there is a spontaneous rearrangement of monochloroethylene oxide to monochloroacetaldehyde. We have therefore had an interest in finding whether a spontaneous ring–opening process for propylene oxide exists or not.

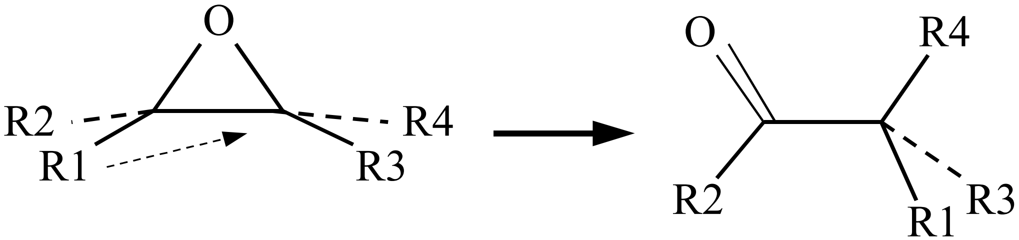
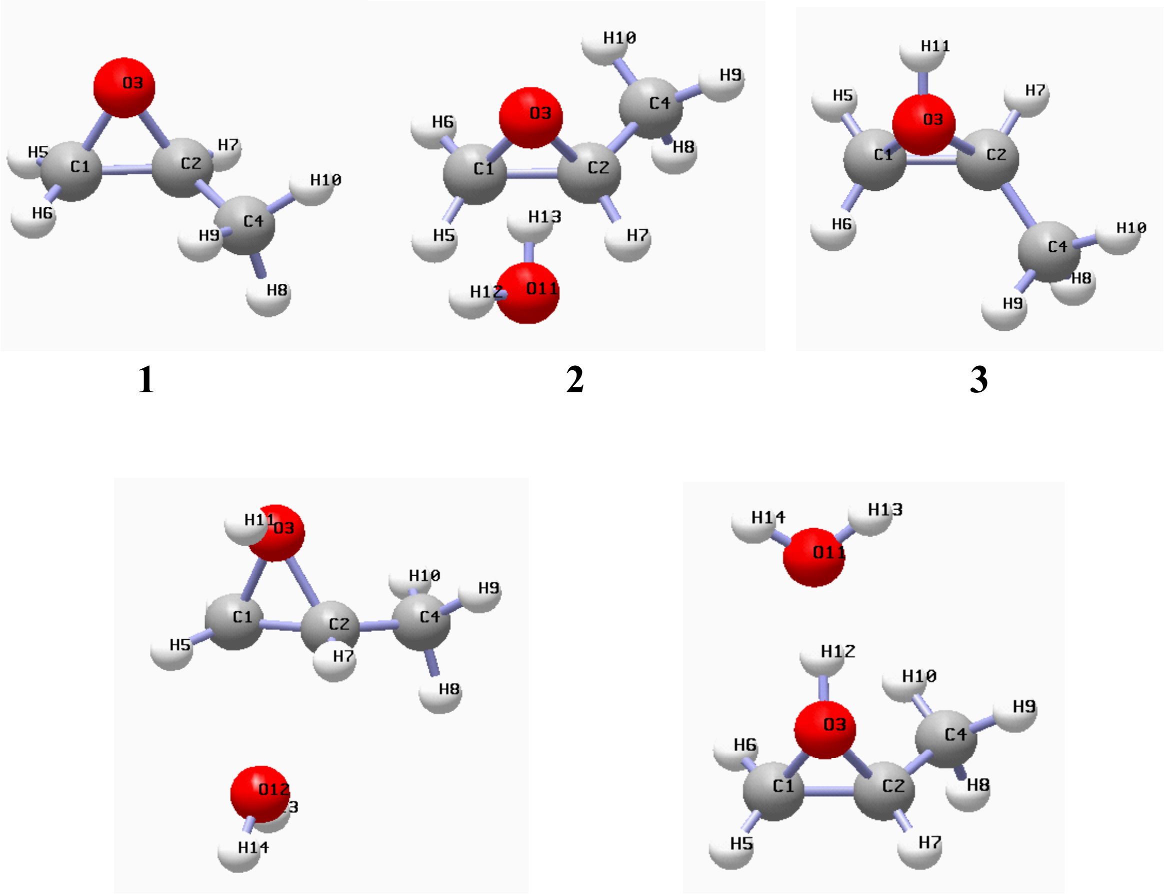


Chart I

In the present study we investigated the energy changes with C–O bond stretching for five systems, namely an isolated propylene oxide **1**, a hydrated propylene oxide **2**, a protonated propylene oxide **3**, a protonated and hydrated propylene oxide **4**, and a propylene oxide with a hydronium ion **5**, by quantum chemical calculations using the MP2/6–31G** level. In these systems the solvent molecules were not taken in account in the calculations though the systems, except **1**, were constructed based on imagining the aqueous solution. Localized molecular orbitals were calculated for systems **1**, **3**, and **4**. The transition states of the ring–opening reactions for **1**, **3**, and **4** were searched and the IRC calculations with them were performed.

2 METHODS OF CALCULATION

All calculations were performed using the MP2/6–31G** level of calculations in the Gaussian98 program [21] installed on an SGI–Origin–3400 computer of Toyama Medical and Pharmaceutical University. The only one exception is the optimizations of **1** which was performed using MP2/6–31++G**, MP3/6–31G**, MP3/6–31++G**, and QCISD/6–31G** levels. Localized molecular orbitals have been obtained by the Boys' method in Gaussian98.



1 **2** **3**

4 **5**

Figure 1. Stable structures of **1**–**5** calculated by the MP2/6–31G** method and the numbering of atoms. **1**: an isolated propylene oxide; **2**: a hydrated propylene oxide; **3**: a protonated propylene oxide; **4**: a protonated and hydrated propylene oxide; **5**: a propylene oxide with a hydronium ion.

3 RESULTS AND DISCUSSION

3.1 Optimized Structures and Charge Densities of Propylene Oxides

The optimized structures of **1**–**5** at the MP2/6–31G** level are shown in Figure 1. The numbering of atoms in each compound is also shown in the figure, and the heavy atoms at the same positions in **1**–**5** have been assigned the same numbers. Although in the initial geometry of **5** a hydronium ion was placed close to the epoxide oxygen atom, the optimized structure in the figure has been found to be like a water molecule binding to the hydrogen atom of **3**. The optimized geometrical parameters of the oxide ring are listed in Table 1. The results in the table reveal that the lengths of the C–O bonds in neutral and cationic compounds differ from each other. The lengths of the C–O bonds in **1** and **2** were found to be 1.44 to 1.45 Å, while they were 1.52 to 1.57 Å in **3** and **4**. The lengths of the C–O bonds in **5** were found to be between these values. It was found in common through **1**–**5** that the length of a C–O bond involving a carbon atom binding to a methyl residue is greater than that of another C–O bond in the same compound. On the other hand, variations in the lengths of the C_2–C_4 bonds in **1**–**5** show the opposite tendency to those of the C–O bonds. That is, the lengths of the C_2–C_4 bonds in neutral compounds of **1** and **2** are longer than those in protonated compounds of **3**, **4** and **5**.

Table 1. The main geometrical parameters of propylene oxide.

	1	**2**	**3**	**4**	**5**
bonds (Å)					
C_1–C_2	1.4648	1.4631	1.4611	1.4485	1.4610
C_1–O_3	1.4413	1.4516	1.5206	1.5443	1.4980
C_2–O_3	1.4411	1.4530	1.5613	1.5699	1.5223
C_2–C_4	1.5006	1.4990	1.4860	1.4847	1.4930
angles (°)					
C_1–C_2–O_3	59.46	59.71	60.30	61.39	60.24
C_2–C_1–O_3	59.45	59.80	63.12	63.18	61.91
C_1–C_2–C_4	121.81	122.02	123.18	122.9	122.75

Table 2. Total atomic charges of heavy atoms in propylene oxide by Mulliken's population analysis for optimized structures of **1**–**5** (**5'**) and atomic charges with hydrogens (au).

	1	**2**	**3**	**4**	**5(5')**
Total atomic charges					
C_1	–0.0251	–0.0381	–0.0389	–0.0029	–0.0484(–0.0484)
C_2	0.1103	0.0975	0.0592	0.0896	0.0835(0.0826)
O_3	–0.4681	–0.4906	–0.3886	–0.4161	–0.4594(–0.4556)
C_4	–0.3482	–0.3477	–0.3708	–0.3698	–0.3940(–0.3931)
Atomic charges with hydrogens [a]					
C_1	0.2137	0.2301	0.4512	0.4588	0.3928(0.3939)
C_2	0.2316	0.2508	0.2966	0.3123	0.3136(0.3038)
O_3	–0.4681	–0.4906	0.0389	0.0013	0.0240(0.0283)
C_4	0.0228	0.0334	0.2135	0.1882	0.1437(0.1434)

[a] Sum of atomic charges of a heavy atom and the hydrogen atoms binding the heavy one.

The atomic charges obtained from Mulliken population analysis are listed in Table 2. These results indicate that only C_2 carbon in each compound has a positive charge, while other heavy atoms have a negative charge. It can be inferred from the electrostatic interactions that the C_1–O_3 bond is weaker than the C_2–O_3 bond. On the basis of the results it may be said that the propanone derived from the C_1–O_3 bond breaking is produced more than the propanal derived from C_2–O_3 bond breaking is. Dubnikova and Lifshitz [17] have performed DFT calculations of propylene oxide and have derived the same situation. That is, the activation energy of a C_1–O_3 bond breaking producing a propanone is lower than that of a C_2–O_3 bond breaking producing propanal. On the other hand, Flowers [13] has measured the products from the gas phase decomposition of propylene oxide, determining the activation energies needed to produce propanone and propanal. The results show that the activation energy to produce propanone is larger than that to produce propanal. Lifshitz and Tamburu [14] have come to a similar conclusion based on experiments using a single–pulse shock tube. Long and Lifshitz [22] have used mass spectrometry to measure the hydrolysis products from propylene oxide and isobutylene oxide, finding that the C–O bond breaking in a neutral solution show the same tendencies as those just described above. In an acidic solution, however, it was found that a C_2–O_3 bond is broken more easily than a C_1–O_3 bond.

In Table 2 the atomic charges with hydrogens summed into heavy atoms are shown. It was found that the atomic charge of an epoxide oxygen atom depends on the total molecular charge. In the neutral systems of **1** and **2**, the oxygen charge is negative, while in the cationic systems of **3**, **4**, and **5**, it is positive. The atomic charges for hydrogens bonded to carbon atoms are all positive. These results imply that breaking of the C–O bond in protonated systems occur more easily than those in neutral systems.

Table 3. Dependency of the geometrical parameters and charge densities in **1** on the calculating methods.

	MP2		MP3		QCISD
	6–31G**	6–31++G**	6–31G**	6–31++G**	6–31G**
bond lengths (Å)					
C_1–C_2	1.4648	1.4666	1.4679	1.4697	1.4677
C_1–O_3	1.4413	1.4484	1.4308	1.4346	1.4368
C_2–O_3	1.4411	1.4474	1.4298	1.4328	1.4357
C_2–C_4	1.5006	1.5007	1.5042	1.5046	1.5055
Total atomic charge (au)					
C_1	–0.0251	–0.0421	–0.0063	–0.0101	–0.0022
C_2	0.1103	0.0489	0.1198	0.0684	0.1211
O_3	–0.4681	–0.3841	–0.4899	–0.3958	–0.4873
C_4	–0.3482	–0.4115	–0.3325	–0.3912	–0.3231
Atomic charges with hydrogens (au) [a]					
C_1	0.2137	0.1986	0.2256	0.2083	0.2248
C_2	0.2316	0.1843	0.2382	0.1912	0.2370
O_3	–0.4681	–0.3841	–0.4899	–0.3958	–0.4873
C_4	0.0228	0.0012	0.0261	–0.0037	0.0254

[a] See footnote [a] in Table 2.

In order to investigate the influences of basis sets and electronic correlations on geometrical parameters and atomic charges, we carried out calculations for **1** at the MP2/6–31++G**, MP3/6–31G**, MP3/6–31++G**, and QCISD/6–31G** levels. The results obtained from these calculations are listed in Table 3. The differences of bond lengths between several methods are small in comparison with the differences between the several systems in Table 1. For examples, the difference in C_2–O_3 bond lengths in Table 1 is 0.1288 Å, while that in Table 3 is 0.0176 Å. In the case of atomic charges for hydrogens, a similar tendency is shown in the results of Tables 2 and 3.

Regarding the usual atomic charges, however, we found no identifiable trend. These results suggest that sophisticated calculations are not needed to qualitatively investigate the structures and atomic charges for these systems.

3.2 C–O bond breaking

Figure 2 shows the energy variations with respect to the C_2–O_3 bond stretching of epoxide for **1**–**5** and **5'**. **5'** means the SCRF calculations of **5**. It can be seen from the figure that the energy variations of **5** and **5'** are slightly different from each other, suggesting that using the reaction fields in calculating the ring–opening potentials does not bring about meaningful changes in the potentials. Therefore **5'** is excluded from consideration in all of the discussion below. A lowering of energy was shown only at the C_2–O_3 distance of 2.2 Å in **4**. In no other cases shown in this figure was a lowering of energy observed. The increases in the energies of **3**, **4** and **5** with increases in the C_2–O_3 bond lengths are less steep than those of **1** and **2**. The energy variations of **1**–**5** are consistent with the data in Table 2. That is, from the perspective of electrostatic interactions, the C_2–O_3 bonds in cationic systems are weaker than those in neutral systems.

Three **3**, **4**, and **5** systems are protonated cationic cases. Only **4** among them demonstrated a decrease of energy at a C_2–O_3 bond length of 2.2 Å. To identify differences between **3** and **4** and between neutral and acidic solutions, localized molecular orbital calculations were carried out for **1**, **3**, and **4**. The localized molecular orbitals (LMOs) related to C_1–O_3 and C_2–O_3 bonds for **1**, **3**, and **4** are shown in Figures 3, 4, and 5, respectively.

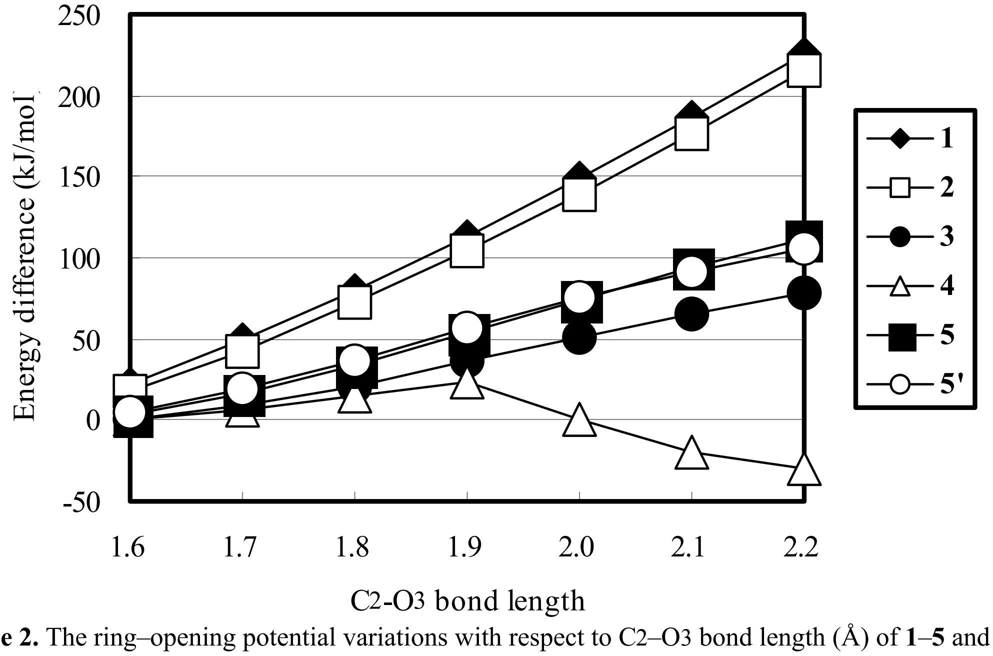


Figure 2. The ring–opening potential variations with respect to C2–O3 bond length (Å) of **1**–**5** and **5'**.

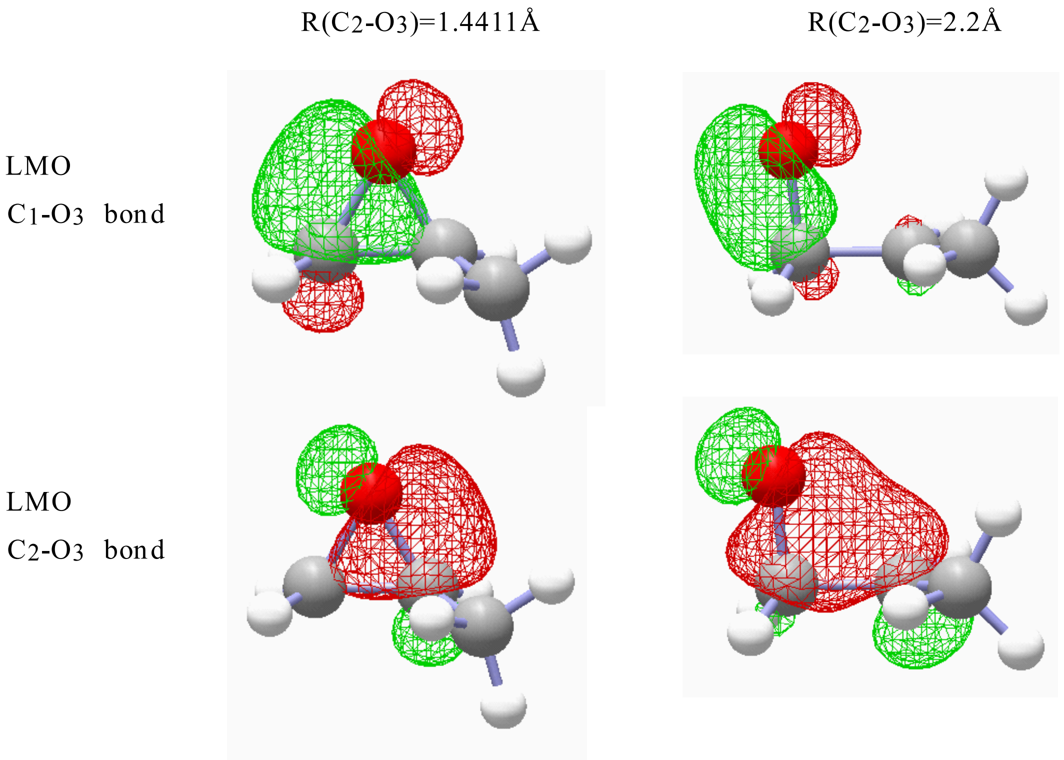


Figure 3. The localized molecular orbitals (LMOs) on C_1–O_3 and C_2–O_3 bonds of **1** at lengths 1.4411 and 2.2 Å of the C_2–O_3 bond.

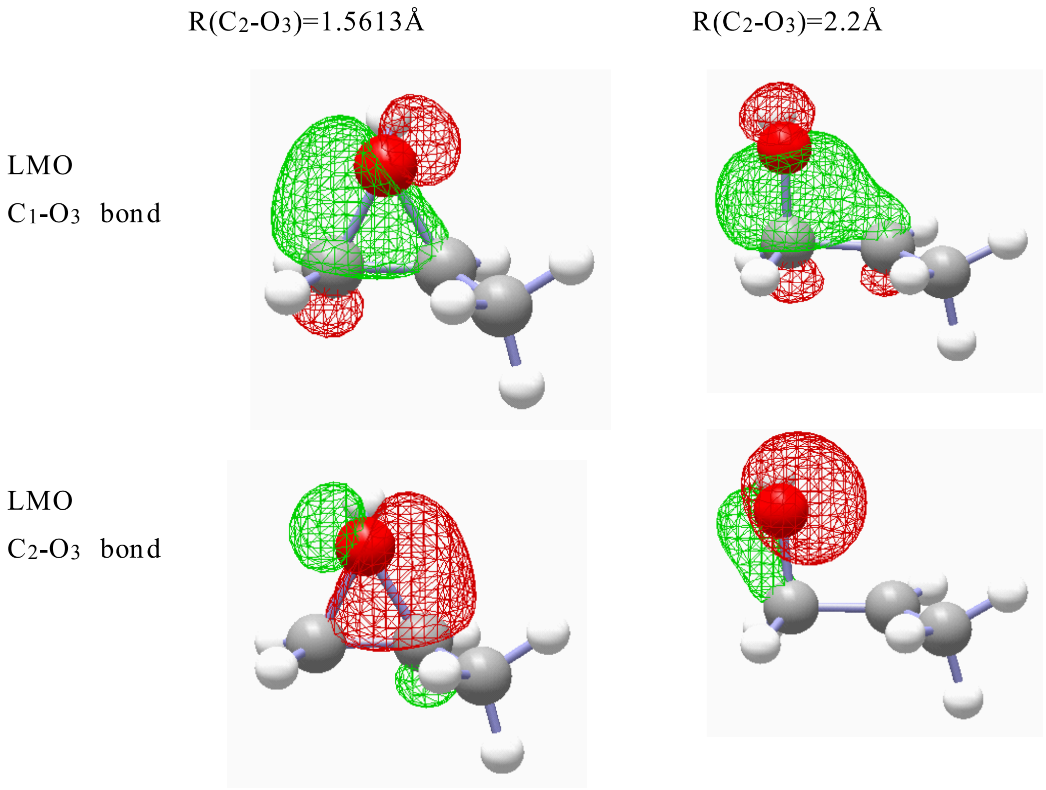


Figure 4. The localized molecular orbitals (LMOs) on C_1–O_3 and C_2–O_3 bonds of **3** at lengths 1.5613 and 2.2 Å of the C_2–O_3 bond.

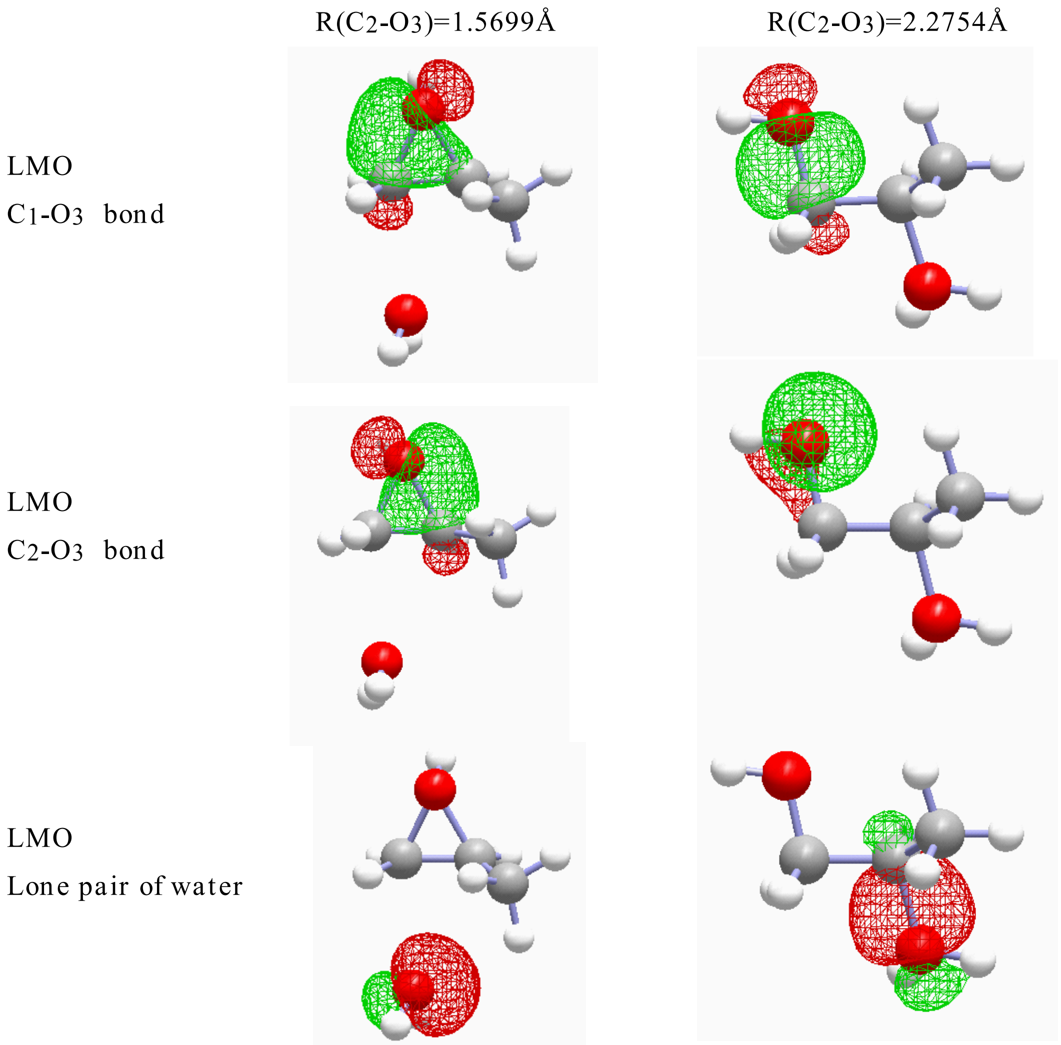


Figure 5. The localized molecular orbitals (LMOs) on C_1–O_3 bond, C_2–O_3 and lone pair orbital of water of **4** at lengths 1.5699 and 2.2754 Å of the C_2–O_3 bond.

A lone pair orbital of the oxygen atom in a water molecule is shown in Figure 5. LMO localized on a C_1–O_3 bond is expected to be invariable through cleavage of the C_2–O_3 bond. On the other hand, the LMO on the C_2–O_3 bond is expected to transform to a lone pair orbital of the oxygen atom through this cleavage. It can be seen in Figure 3 that even when the C_2–O_3 bond length is 2.2 Å, the LMO on the C_2–O_3 bond never transforms to a lone pair orbital. In contrast, in Figure 4 it is shown that the LMO localized on a C_2–O_3 bond does become the lone pair orbital of an oxygen atom. It can also be seen in the figure that the LMO localized on the C_1–O_3 bond expands into a C_2 atom when the C_2–O_3 bond length is 2.2 Å. In each case there is one LMO which hinders the C_2–O_3 bond cleavage making cationic site of C2 atom which has a low valence. It is shown from Figure 5 that when the length of the C_2–O_3 bond is 2.2754 Å, the LMO on the C_2–O_3 bond is transformed into a lone pair orbital of an oxygen atom. It is also shown that the LMO on the C_1–O_3 bond is scarcely expanded to a C_2 atom. One important situation in Figure 5 is the conversion of a lone pair orbital of the oxygen atom in the water molecule to a new bond to a C_2 carbon atom when the C_2–O_3 bond is 2.2754 Å. The LMOs in **4** when the C_2–O_3 bond length is 2.2754 Å have forms almost identical to the LMOs when the length is 2.2 Å. The C_2–O_3 bond length is 2.2754 Å for the fully optimized structure obtained from the calculation starting with the initial structure of 2.2 Å. The results of the LMO calculations indicate that the low valence of the C_2 atom hinders the breaking of the C_2–O_3 bond. It also appears that the existence of a nucleophilic reagent complementing the valence accelerates the ring–opening reaction.

3.3 IRC calculations

One of our interests is the reaction path of making propanal through the ring–opening of a propylene oxide. In order to complete the process of producing a propanal from a propylene oxide, one of the hydrogen atoms binding to a C_1 atom of propylene oxide must transfer to a C_2 atom. Dubnikova and Lifshitz [17] have concluded that both the ring–opening process of propylene oxide and the hydrogen transfer process proceed via concerted mechanisms in neutral gas phase conditions. Coxon *et al.* [18], however, have concluded that in protonated propylene oxide, two processes occur in concerted asynchronous process.

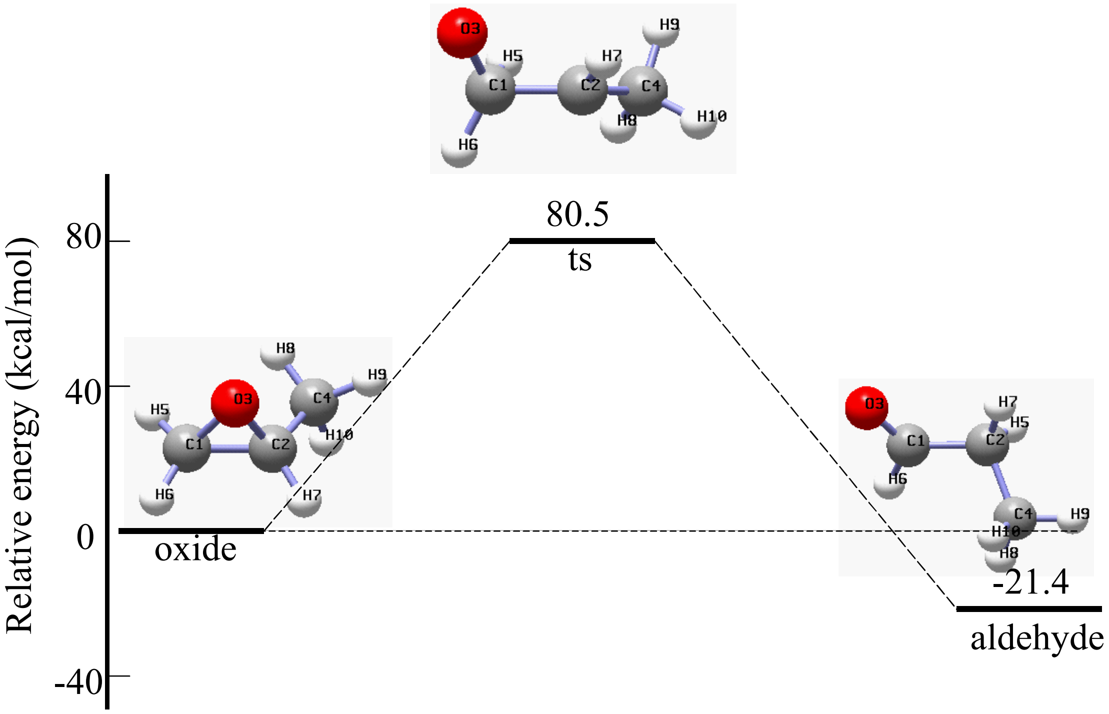


Figure 6. Relative energy diagram of reactant (oxide), ts, and product (aldehyde) for **1**.

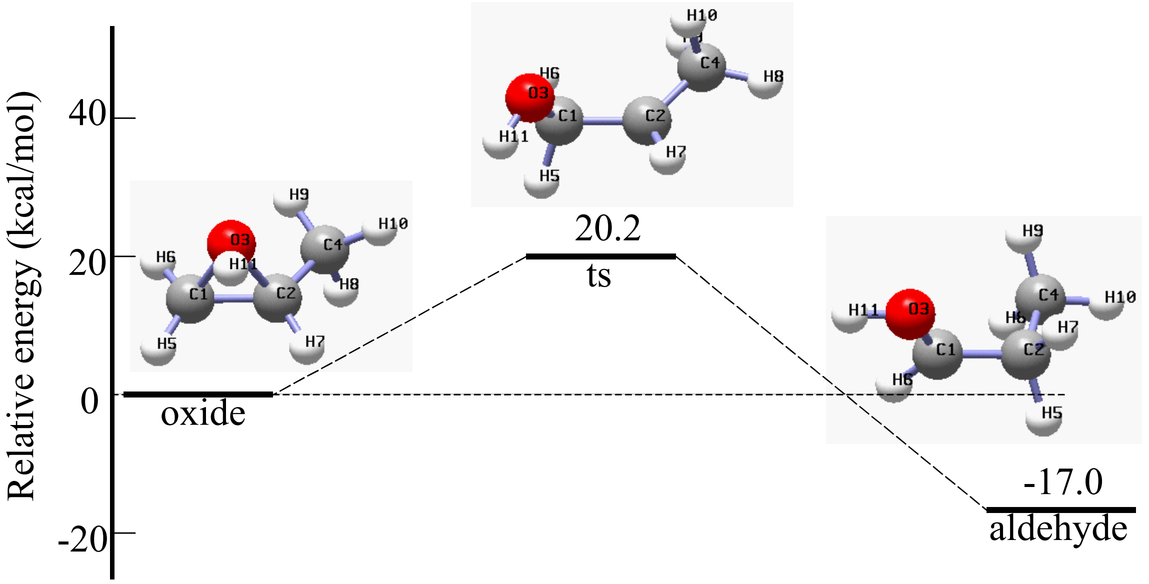


Figure 7. Relative energy diagram of reactant (oxide), ts, and product (aldehyde) for **3**.

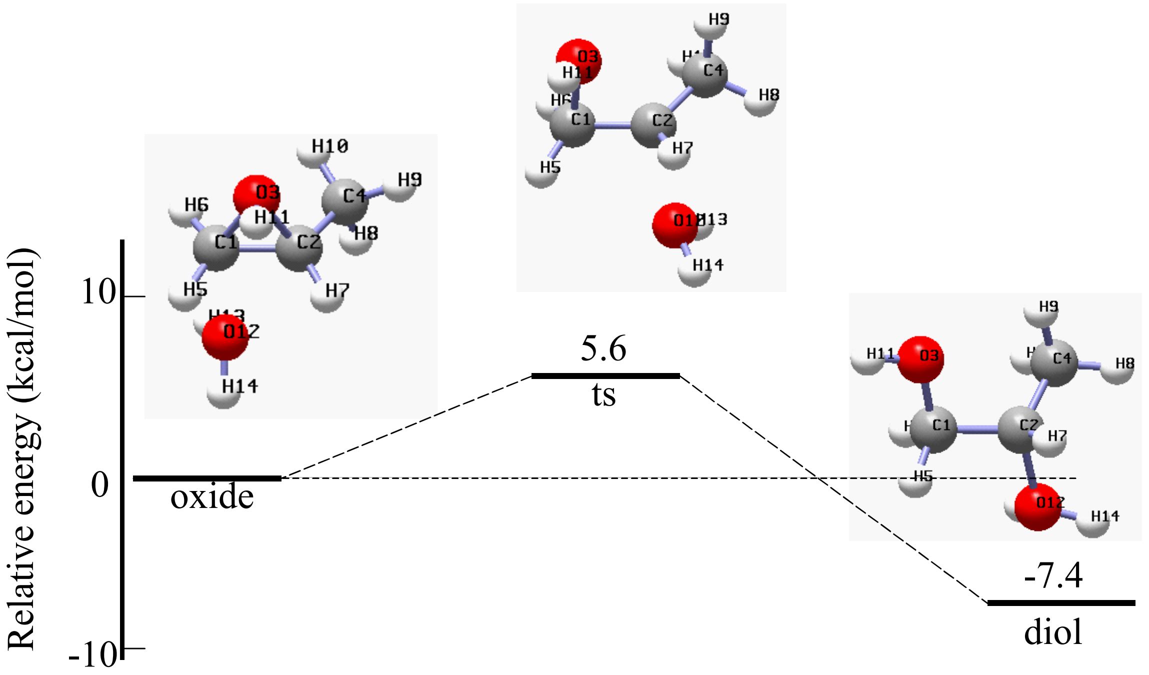


Figure 8. Relative energy diagram of reactant (oxide), ts, and product (diol) for **4**.

The IRC calculations at the MP2/6–31G** level have been performed for the ring–opening potentials of **1**, **3**, and **4**. The results are shown in Figures 6, 7, and 8, respectively. The calculated activation energies of **1**, 80.5 kcal/mol, is fairly large in comparison with the experimental one, 58.5 kcal/mol [13,14], and the theoretical one with CCSD(T)/cc–pVDZ//B3LYP/cc–pVDZ level, 54.99 kcal/mol [17]. The final product was propanal as shown in Figure 6 [17]. The calculated activation energy of **3** is 20.2 kcal/mol as shown in Figure 7.

It is somewhat larger than those of the experimental one, 18.62 kcal/mol [16], and of the theoretical result with 6–31G* basis set, 17.7 kcal/mol [18]. The final product in the reaction was also the protonated propanal, and this is also coincided in Ref. [18]. The activation energy of **4**, 5.6 kcal/mol, is very small in comparison with those of **1** and **3** and the C_2–O_3 bond breaking of **4** derived a diol–type product as shown in Figure 8. This is reflected the result of **4** in Figure 2 in which in the process of ring–opening of **4**, a water molecule binds the C_2 atom. As such, the transfer of a hydrogen atom from the C_1 atom to the C_2 atom may not be preferred over the approach of a water molecule to the C_2 atom.

It is found from Figures 6 and 7 that the transfer of H_5 from C_1 atom to C_2 atom occurs in the results of IRC calculations for the ring–opening reactions of **1** and **3**. The distance of C_2–H_5 bond changes from 2.2057 Å of oxide for **1** to 1.0937 Å of aldehyde via 1.7763 Å at the transition state. On the other hand, for **3** the distances at the stationary points are 2.2147, 1.0921, and 2.1039 Å, respectively. For **3** it is obvious that the transfer of a hydrogen atom does not begin until the reaction goes over the transition state. This coincides to the conclusion of reference [18]. From the consideration of the results obtained in this study and listed in several references described above it is found that the reaction paths obtained from the different levels of calculations are slightly different each other though the heights of energy barrier vary with the basis sets and the electronic correlations.

4 CONCLUSIONS

Quantum chemical calculations were performed for the C–O bond stretching of propylene oxide in five systems: an isolated propylene oxide, a hydrated propylene oxide, a protonated propylene oxide, a protonated and hydrated propylene oxide, and a propylene oxide with a hydronium ion. The aim of these calculations was to reveal what conditions allow spontaneous completion of the ring–opening process of propylene oxide to create a propanal. Two conclusions can be drawn from our results. The first is that the ring–opening process never proceeds spontaneously under the conditions considered in this study. The second conclusion, drawn from the IRC calculations of **1** and **3**, is that both the ring–opening process and the hydrogen transfer process occur in a one–step reaction and that the reaction paths are slightly affected by the level of basis set and electronic correlation used in the calculation. The results of the localized molecular orbitals calculations reveal that the low valence of the carbon atom of a breaking C–O bond hinders the C–O bond breaking.

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