

Ab Initio Investigations of Some 1, 2-Diols Rearrangement Via G3 Calculations

Mustafa R. Helal* and Khamis A. Abbas

Department of Chemistry, Yarmouk University, Irbid, Jordan

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Abstract

Conformational analysis of protonated of 1,2-ethanediol, 1,2-propanediol and 2-methyl-1,2-propanediol had been studied and the resulting rotational transition states had been determined. The transition states that result from the proton transfer from 2°- and 3°-OH groups (M1) to 1°-OH group (M2) had been also determined. It had been found that the equilibrium favors M1 formation. This result is agreeable with the published data. The possible mechanisms for the rearrangement of M1 to the corresponding aldehyde had been discussed. The obtained G3 results had been compared with the published theoretical and experimental results. It had been found that G3 method excludes the two-steps mechanism in contrast to other calculations with lower level. The possibility of formation of epoxides as by-products had been also discussed.

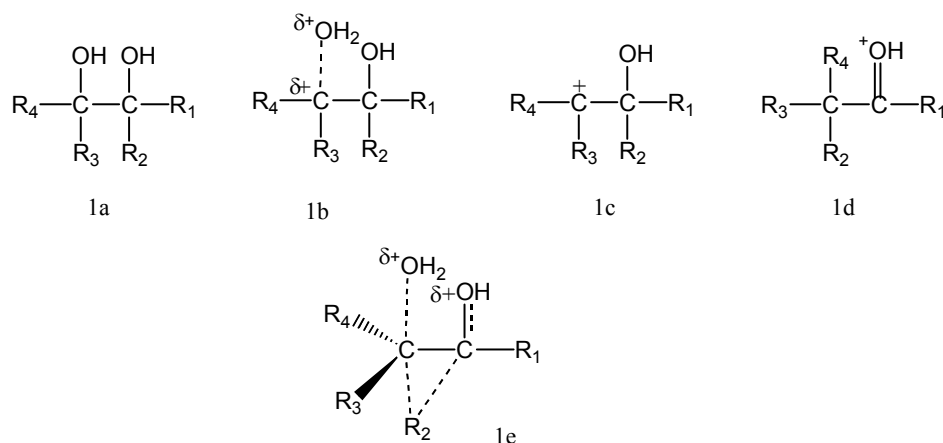
Keywords: Protonated 1,2-Diols; 1,2-Diols Rearrangement; Conformation; G3 calculations.

Introduction

Several aspects about pinacol-pinacolone rearrangement reactions attracted and still attract the attention of researchers. Some of these aspects are organic synthesis [1-7], the migratory aptitude for different groups [8-10] and the mechanism of this type of rearrangement. The later aspect had been experimentally and theoretically studied [8, 11-13]. The present work focuses on the mechanism, and the published data about mechanisms are going to be discussed below.

There are two possible mechanisms for pinacol-pinacolone rearrangement: the two-steps and the concerted mechanisms (Scheme 1). The two-steps mechanism is that in which the protonated diol (1b) loses water to form a carbocation (1c) as an intermediate. Then, R₂ migrates to yield the protonated carbonyl compound (1d). In the concerted mechanism, the migration of R₂ and the loss of H₂O occur simultaneously forming the bridged transition state (1e) which converts to (1d). The formation of the carbocation is usually accompanied by racemization in chiral substrates while inversion indicates concerted mechanism.

* Corresponding author. E-mail: Mustafa_helal@yahoo.com



Scheme 1: 1a, 1b, 1c, 1d and 1e represent the structures of pinacol, protonated pinacol, carbocation, protonated carbonyl compound and R₂-bridged transition state; respectively.

The published results^[8, 11, 12] indicated that the two-steps mechanism, may occur in polar solvents, while the concerted mechanism predominates in nonpolar solvents and the gas phase. However, using Fe-substituted molecular sieves as catalyst in toluene favors the formation of carbocations in pinacol-pinacolone rearrangement^[14]. The two-steps mechanism also predominates in solid state reactions^[15].

G3 calculations of the rearrangement of 2, 3-dimethylbutane-2,3-diol requires special computational facilities and very long computation time since it has eight heavy atoms. Therefore, most of the workers in this field investigate smaller diols as models for pinacol-pinacolone rearrangement even at lower level than G3. The rearrangements of H₂O⁺CH₂CH₂OH, CH₃CH⁺OH₂CH₂OH and (CH₃)₂C⁺OH₂CH₂OH had been investigated via ab initio calculations using RHF/6-31G optimized geometries and RHF/6-31G** for energy calculations. i. e. RHF/6-31G**// RHF/6-31G^[13]. The reported energy values required for the formation of the 1^o, 2^o and 3^o carbocations are 48.7, 32.4 and 20.4 kcal/mol; respectively, while those necessary for the formation of H-bridged transition states in 1^o, 2^o and 3^o protonated hydroxyl groups are 23.6, 19.7 and 16.7 kcal/mol; respectively^[13]. The energy differences between the two paths are 25.1, 12.7 and 3.7 kcal/mol for 1^o, 2^o and 3^o species, respectively^[13]. The conclusion of the authors was that the concerted mechanism predominates in the three species^[13]. This conclusion is true for 1^o and 2^o species because the values of energy differences between the two paths are relatively large. However, the energy difference, 3.7 kcal/mol, is relatively small. Therefore, no conclusive conclusion could be drawn from RHF results for 3^o species. Consequently, this work was initiated to study the rearrangement mechanism in 3^o species using basis sets of higher level.

The second purpose of the present work is studying the possibility of the formation of epoxides in pinacol rearrangement. The most of the published works had

been focused on the formation of carbonyl compounds. However, it had been reported that epoxide intermediates are formed in some pinacolic rearrangements^[16].

Computational Details

The computations have been carried out using Gaussian 03 program package, version D.01^[17]. The geometries of all species had been fully optimized at MP2 (full)/6-31G (d) and the G3-enthalpies for each species had been calculated. The G3-enthalpies for the transition states were calculated via a procedure described in Ref. 18. Relaxed potential energy surface (PES) scans are carried out at MP2 (full)/6-31G (d) level to determine the stationary points then quadratic synchronous transit algorithm (QST)^[19] was further carried out at MP2 (full)/6-31G (d) level to confirm that the transition states connect the right minima. Then, each stationary point, obtained via scanning and confirmed by QST, had been fully optimized as TS at MP2(FULL)/6-31G(d). Natural bond orbital, NBO, analysis had been also done at MP2 (full)/6-31G (d) level of theory.

Results and Discussion

The protonation of any hydroxyl group of 1, 2-ethanediol, HOCH₂CH₂OH, would give the same intermediate due to its symmetry. However, the protonation of either CH₃CHOHCH₂OH or (CH₃)₂COHCH₂OH would produce two intermediates: M1 and M2 (Figure 1). The protonation of the OH bonded to the more substituted carbon gives the more stable intermediate (M1) while the protonation of the other OH gives the less stable intermediate (M2).

Protonated Diols Minima (M1 and M2)

The distinct difference between the three M1 intermediates is the σ_{C2-O4} bond lengths. The lengths of σ_{C2-O4} bonds in 1°, 2° and 3° are 1.505Å, 1.530 Å and 1.553 Å, respectively (figure 1). The σ_{C2-O4} bond is anti to σ_{C1-H8} as shown in figure 1. NBO analysis shows that the σ bond of the anti hydrogen overlaps with σ^*_{C2-O4} bond. This overlapping causes in lengthening of σ_{C2-O4} . As the numbers of anti hydrogen atoms increase, the length of σ_{C2-O4} bond increases. The numbers of the anti σ_{C-H} bonds are 3, 2, and 1 in 3°, 2°, and 1° protonated diols, respectively.

Mulliken atomic charges on C₂ are 0.187, 0.062 and -0.088 in 3°, 2°, and 1° of M1 species; respectively. This means that 3° species could be considered as a hydrated carbocation and the 2° species to a lesser extent. The steric interaction between H₂O molecule and methyl group(s) on C₂ keep H₂O away from C₂. C₂ in 3° and 2° are bonded to two and one methyl groups, respectively. Thus, more steric interaction is found in 3° and σ_{C2-O4} is the longest.

Figure 1 shows that the σ_{C1-O3} bond lengths in sec- and tert-M2, O₃ is the protonated oxygen, are 1.499Å and 1.503Å; respectively. Both bonds have approximately same length due to the absence of carbocation character in C₁. Mulliken

atomic charges on C₁ of M2 are -0.064 and -0.073 in 3° and 2°; respectively. It is known that 1° carbocations are relatively unstable.

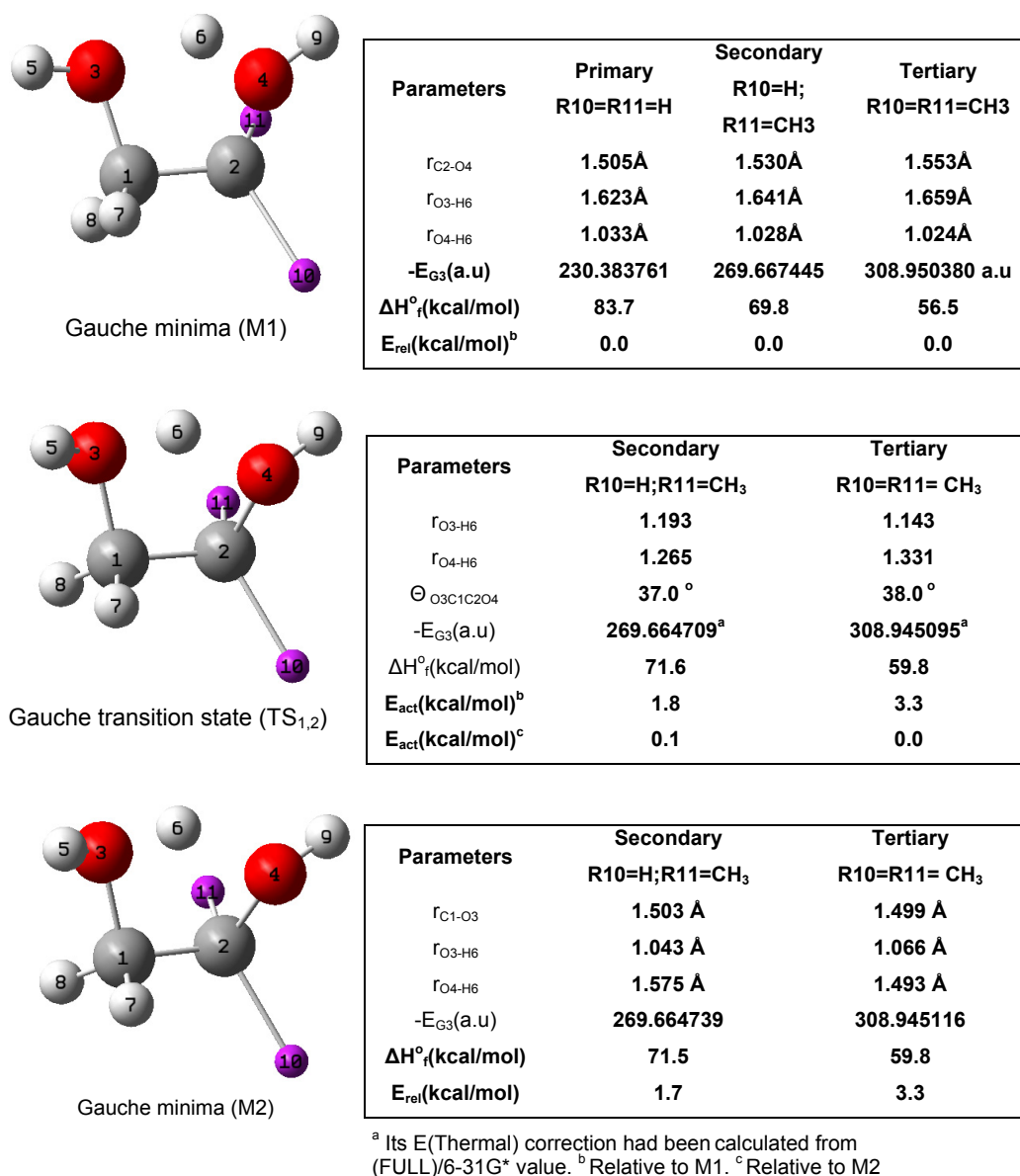


Figure 1: MP2 (FULL)/6-31G* Optimized key geometrical parameters, G3-Enthalpy, ΔH_f^o and E_{rel} values of M1, TS_{1,2} and M2.

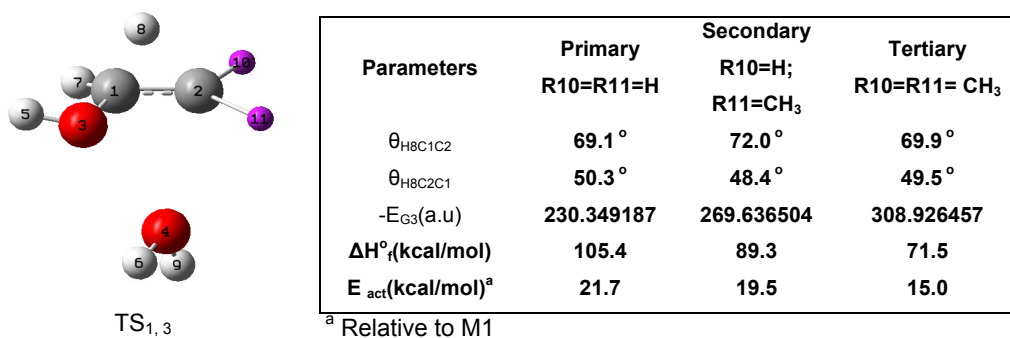
Migration of H₆ from O₄ to O₃ converts M1 to M2 passing through the transition state TS_{1,2} (figure 1). The values of the activation energy, E_{act}, for these transformations are 1.8 and 3.3 kcal/mol in 2° and 3° species; respectively. However, E_{act} values are 0.1 and 0.0 kcal/mol for going from M2 to TS_{1,2} in 2° and 3° species; respectively (Figure 1). This means that there is a fast equilibrium between M1 and M2. The equilibrium favors the formation of M1. The values of dihedral angle θ_{O3C1C2O4} are 37.0 ° and 38.0 ° in sec- and tert- TS_{1,2}; respectively (figure 1). This means that TS_{1,2} exists nearly in gauche conformer.

Rearrangement Mechanisms of M1

It had been mentioned in the introduction that there are two possible mechanisms for the rearrangement of a protonated diol to an aldehyde. These mechanisms are the concerted and the two-steps mechanisms. The concerted mechanism will be discussed first.

The Concerted Mechanism

The concerted mechanism has one transition state. Migration of H₈ in M1 from C₁ to C₂ gives H-bridged transition state (TS_{1,3}) with relatively large E_{act} values. These values are 21.7, 19.5 and 15.0 kcal/mol for 1^o, 2^o and 3^o; respectively, as obtained via G3 method (figure 2a). The RHF/6-31G**//RHF/6-31G corresponding reported values are 23.6, 19.6 and 16.7 kcal/mol; respectively^[13]. The G3 values are lower by 1.9 and 1.7 kcal/mol for 1^o and 3^o transition states; respectively. Both sets are summarized in figure 2b. For 2^o transition state, G3 and RHF methods give approximately the same value. The values of θ_{H8C1C2} and θ_{H8C2C1} (figure 2a) indicate clearly that the transition states have H-bridged structure. The values of the activation energies lead to conclude late transition states. This means that the transition state structure are similar to those of the products, Hammond postulate^[15]. However, the bridged hydrogen, H₈, is closer to C₁. For example, the $r_{\text{C1-H8}}$ and $r_{\text{C2-H8}}$ length values are 1.213Å and 1.543Å for 2^o species, respectively (Appendix).



H-Bridged transition states

Figure 2a: MP2 (FULL)/6-31G* Optimized key geometrical parameters, G3-enthalpy, ΔH_f° , and E_{rel} Values of H-bridged TS

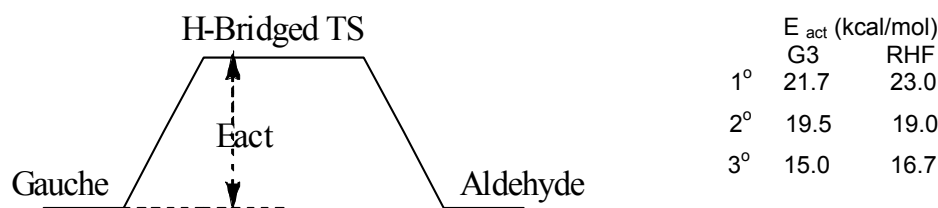


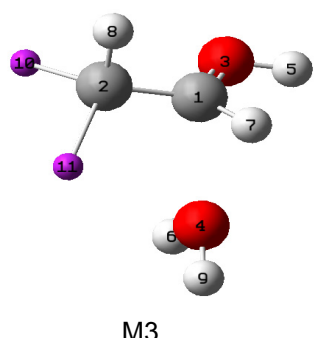
Figure 2b: Potential energy surface, PES, for the rearrangement of M1 to hydrated protonated aldehyde minima (M3)

Hydrated Protonated Aldehydes Minima (M3)

The optimized geometrical parameters and the energies of hydrated protonated aldehydes (M3) are shown in figure 3. NBO analysis shows the presence of a complete double bond between C_1 and O_3 in 3° and 2° species and a partial double bond in 1° . This is reflected in the lengths of $r_{C_1-O_3}$ bonds (figure 3). The lengths of C_1-O_3 bonds are 1.319 Å, 1.278 Å and 1.279 Å in 1° , 2° and 3° ; respectively. The lengths of C_1-C_2 bonds in 1° , 2° and 3° of M3 species are 1.484 Å, 1.464 Å and 1.465 Å; respectively (figure 3). The shortness of C_1-C_2 bonds in 2° and 3° could be attributed to the hyperconjugation, HC, between $\sigma_{C_2-H_8}$ and $\pi^*_{C_1-O_3}$ as indicated by NBO analysis. This overlapping also causes in lengthening of C_2-H_8 bonds and decreasing the values of $\Theta_{H_8C_2C_1}$ in 2° and 3° species. The values of $r_{C_2-H_8}$ are 1.111 Å and 1.105 Å in 3° and 2° ; respectively (figure 3). These lengths are much longer than that in 1° where it is 1.095 Å. Similarly, the value of $\Theta_{H_8C_2C_1}$ in primary aldehyde is 106.9° which is larger than those in sec- and tert- aldehydes. These values are 102.9° and 100.0° in 2° and 3° species of M3; respectively (figure 3).

It should be noted that the obtained M3 species have bisected configuration as it is clear from the values of the dihedral angles $\theta_{H_8C_2C_1O_3}$ and $\theta_{H_8C_2C_1H_7}$ (figure 3). This bisected configuration allows the overlapping between $\sigma_{C_2-H_8}$ bond and $\pi^*_{C_1-O_3}$ molecular orbital.

It should be also noted that the stabilities of M3 is much more stable than M1 in case of protonated 1,2-ethanediol. E_{rel} of M3 is -11.2 kcal/mol (figure 3). E_{rel} of M3 decreases to -3.7 kcal/mol in case of protonated of 1,2-propanediol (figure 3). The M3 aldehyde is even less stable than M1 by 1.0 kcal/mol in case of 2-methyl-1,2-propanediol (figure 3). This might be attributed to the stability order of the protonated hydroxyl group where 3° is more stable than 2° and 1° is the least stable.



Parameters	Primary R10=R11=H	Secondary R10=H; R11=CH3	Tertiary R10=R11=CH3
r_{C1-O3}	1.319Å	1.278Å	1.279Å
r_{C1-C2}	1.484Å	1.464Å	1.465Å
r_{H8-C2}	1.095Å	1.105Å	1.111Å
θ_{H8C2C1}	106.9 °	102.9 °	100.0 °
$\theta_{H8C2C1O3}$	-74.0 °	-82.5 °	-89.3 °
$\theta_{H8C2C1H7}$	70.4 °	84.9 °	78.4 °
$-E_{G3}(\text{a.u.})$	230.401568	269.673445	308.948710
$\Delta H_f^\circ(\text{kcal/mol})$	72.5	66.1	57.5
$E_{\text{rel}}(\text{kcal/mol})^a$	-11.2	-3.7	1.0

^a Relative to M1

Figure 3: MP2 (FULL)/6-31G* Optimized key geometrical parameters, G3-enthalpy, ΔH_f° , and E_{rel} values of hydrated protonated aldehyde minima (M3).

The Two-Steps Mechanism

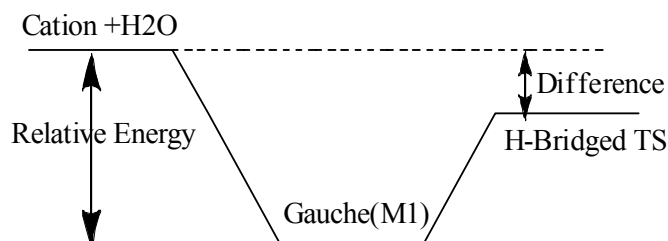
This mechanism involves formation of carbocation as intermediate via dehydration of M1 minima. The produced carbocation should have eclipsed configuration to be capable to rearrange to aldehyde^[13]. Tertiary and secondary carbocations can exist in this conformation^[20, 21] while 1° cannot^[20]. The eclipsed conformer of 1° carbocation is a transition state^[20]. The optimized geometrical parameters of these carbocations are given in References 20 and 21. The G3-enthalpies of the eclipsed isomers of 3°, 2° and 1° carbocations in addition to water are given in Table 1. From the G3 enthalpies of M1 (figure 1) and the data in Table 1, the energy values which are required for the formation of 1°, 2° and 3° carbocations were calculated and found to be 47.8, 32.6 and 22.9 kcal/mol; respectively (figure 4). The figures 2b and 4 indicate that the G3 energy differences between the concerted and the two-steps mechanisms are 26.1, 13.1 and 7.9 kcal/mol for 1°, 2° and 3° species; respectively (figure 4). G3 and RHF^[13] methods agree with each other with respect to 1° and 2° species but differ with respect to 3°. Both methods conclude that the concerted mechanism predominates in 1° and 2° species. However, the possibility of the two-steps mechanism for the 3° species could be excluded according to the G3 energy difference, 7.9 kcal/mol, but could not be excluded according to the RHF value 3.7 kcal/mol.

Table (1): G3-Enthalpies and enthalpies of formation, ΔH_f° , of β - Hydroxy 1 $^\circ$, 2 $^\circ$ and 3 $^\circ$ carbocations and H₂O.

Eclipsed R ⁺	G3 ^a	
	Enthalpy (a. u.)	ΔH_f° ^b
HOCH ₂ CH ₂ ⁺	-153.929332	187.5
HOCH ₂ CHCH ₃ ⁺	-193.237248	158.5
HOCH ₂ C ⁺ (CH ₃) ₂	-232.535632	135.4
H ₂ O	-76.378261	

^a The G3 values had been taken from References 18 and 19.

^b Units are in kcal/mol.



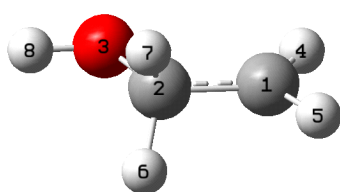
	E _{rel} (kcal/mol)		Difference (kcal/mol)	
	G3	RHF	G3	RHF
1 $^\circ$	47.8	48.7	26.1	25.1
2 $^\circ$	32.6	32.4	13.1	12.7
3 $^\circ$	22.9	20.4	7.9	3.7

Figure 4: The G3 energy values required for the formation of the eclipsed conformers of the carbocations from M1 and the energy differences between the formation of carbocations and H-bridged transition states.

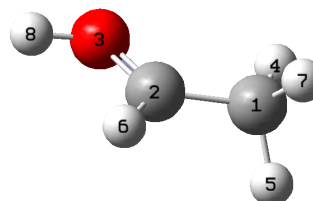
Rearrangement of Carbocations to Protonated Aldehydes

The second step in the two-steps mechanism is the rearrangement of the carbocation to a protonated aldehyde. The eclipsed conformers of β -hydroxyethyl carbocation exists as a transition state and it could rearrange directly to protonated ethanal via migration of H₇ from C₂ to C₁ (figure 5). The 2 $^\circ$ and 3 $^\circ$ carbocations (M4) rearrange to the corresponding protonated aldehydes (M5) through formation of H-bridged transition state, TS_{4, 5}. These transition states are formed by migration of H₅ from C₂ to C₁ (figure 6), with relatively small activation energy values, especially for 2 $^\circ$ carbocation. The G3 E_{act} values are 0.2 and 2.72 kcal/mol, for 2 $^\circ$ and 3 $^\circ$; respectively (figure 6). These activation energy values indicate that the rate determining step in the

two-steps mechanism is the formation of the carbocation rather than the formation of the H-bridged transition state.

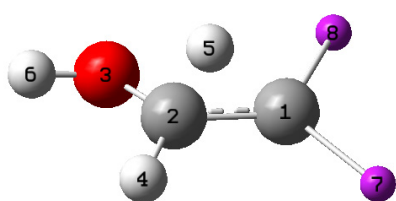


Eclipsed hydroxyethyl carbocation.



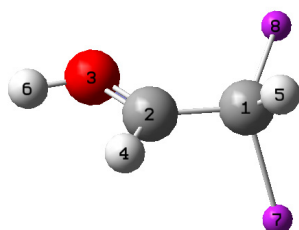
Protonated ethanal

Figure 5: Hydroxyethyl carbocation and protonated ethanal.



H-bridged TS_{4,5}

Parameters	Secondary	Tertiary
	R7=H;R8=CH ₃	R7=R8=CH ₃
θ_{C1C2H5}	89.1°	74.0°
θ_{C2C1H5}	39.3°	46.8°
$-E_{G3}(\text{a.u.})$	193.236926	232.531298
$E_{\text{act}}(\text{kcal/mol})^a$	0.20	2.72



Protonated aldehyde minima
(M5)

Parameters	Primary	Secondary	Tertiary
	R7=R8=H	R7=H; R8=CH ₃	R7=R8=CH ₃
θ_{C1C2H5}	112.2°	105.2°	106.1°
θ_{C2C1H5}	28.4°	31.5°	31.0°
θ_{O3C2C1}	119.5°	119.8°	120.2°
$\theta_{O3C2C1R8}$	0.2°	0.0°	14.3°
$-E_{G3}(\text{a.u.})$	154.001438	193.276853	232.550652
$\Delta H_f^\circ(\text{kcal/mol})$	142.0	134.3	126.0
$E_{\text{rel}}(\text{kcal/mol})^a$	-45.5	-24.2	-9.4

^a Relative to the corresponding carbocation.

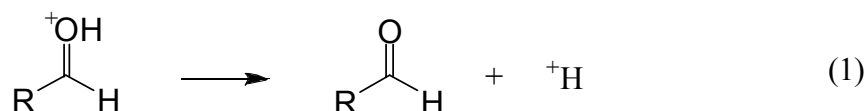
Figure 6: MP2 (FULL)/6-31G* Optimized key geometrical parameters, G3-Enthalpy, ΔH_f° and E_{rel} values of TS_{4,5} and M5.

Protonated Aldehydes (M5)

The optimized geometrical parameters, G3 enthalpies, enthalpies of formation, and relative energy values are shown in figure 6. The methyl groups in secondary and tertiary protonated aldehydes are eclipsed with the carbonyl group as indicated from $\theta_{O3C2C1R8}$ values (figure 6). This structure is the preferred one for aldehydes^[22].

The experimental proton affinities of ethanal, propanal and 2-methylpropanal had been reported to be 188.9, 191.4 and 193.3 kcal/mol^[23]; respectively. However, another experimental value, 184.1 kcal/mol,^[24] had been reported for ethanal. The

calculated proton affinity values, according to equation 1, are 185.8, 188.9 and 190.4 kcal/mol for 1°, 2° and 3°, respectively. The values of both sets, experimental and calculated, correlate well with each other, if the experimental and theoretical uncertainties are taken into consideration. The proton affinity values of these protonated species had been calculated from their ΔH_f° values (figure 6). ΔH_f° values of H^+ for CH_3CHO , CH_3CH_2CHO and $(CH_3)_2CHCHO$ are 368.5 kcal/mol^[23], -40.8 kcal/mol^[27], -45.45 kcal/mol^[25] and -52.25 kcal/mol^[27], respectively.



Epoxides Formation

Epoxides can be formed either from free carbocations or from M1. It had been previously discussed that the formation of free carbocations requires high activation energy. Therefore, the formation of epoxides from carbocations is difficult for the studied molecules. However, aryl diols which can form stable carbocations give epoxides as intermediates^[15].

Epoxides Formation from M1 in Concerted Mechanism

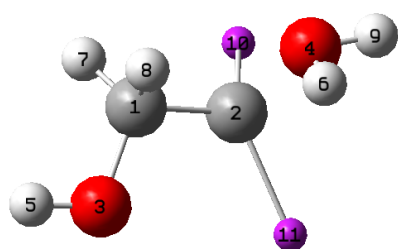
Epoxide is formed from rotational conformer in which OH and $^+OH_2$ are anti to each other, anti conformer, which could be formed from the eclipsed OH//CH₃ and or OH//H transition states.

OH//CH₃ Transition states

Tertiary and secondary species of M1 form OH//CH₃ transition states with relatively high activation energy values, the values are 13.3 and 11.8 kcal/mol for 2° and 3° species; respectively (figure 7). The rotation around C₁-C₂ bond eliminates the intramolecular H-bond which exists in M1. The dihedral angle $\Theta_{O_3C_1C_2R_{11}}$ values are -13.5° and -14.2° in 2° and 3° species; respectively (figure 7). These values are almost twice of those of $\Theta_{O_4C_2C_1H_8}$ values. This could be attributed to the size of CH₃ group comparing to H₈. However, this is not the reason because other data in figure 7 do not support this conclusion as will be seen below. The difference could be attributed to the number of the lone pairs of electrons on O₃ and O₄. O₃ carries two pairs while O₄ has only one pair of electrons. This means that the size of OH is larger than that of $^+OH_2$.

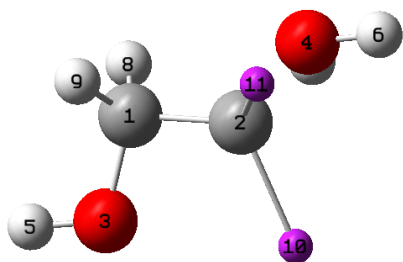
OH//H Transition states

The activation energy values for the formation of OH//H transition state are 12.9 and 11.8 kcal/mol, for 1° and 2°; respectively (figure 7). For 2° species, the activation energy value of OH//CH₃ transition state is higher than that of OH//H transition state by 1.5 kcal/mol (figure 7).



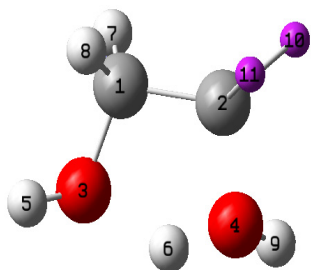
OH//CH₃ TS

Parameters	Secondary R ₁₀ =H; R ₁₁ =CH ₃	Tertiary R ₁₀ =R ₁₁ =CH ₃
Θ _{O4C2C1H8}	-7.7 °	-7.0 °
Θ _{H7C1C2R10}	-1.2 °	0.3
Θ _{O3C1C2R11}	-13.5 °	-14.2 °
-E _{G3} (a.u)	269.646309	308.931627
ΔH ^o _f (kcal/mol)	83.1	68.3
E _{act} (kcal/mol) ^a	13.3	11.8



OH//H TS

Parameters	Primary R ₁₀ =R ₁₁ =H	Secondary R ₁₀ =H; R ₁₁ =CH ₃
Θ _{H9C1C2R11}	-8.0 °	4.0 °
Θ _{O3C1C2R10}	-15.6 °	14.7 °
Θ _{O4C2C1H8}	-9.6 °	5.6 °
-E _{G3} (a.u)	230.363101	269.648748
ΔH ^o _f (kcal/mol)	96.6	81.6
E _{act} (kcal/mol) ^a	12.9	11.8



O//O TS

Parameters	Primary R ₁₀ =R ₁₁ =H	Secondary R ₁₀ =CH ₃ ; R ₁₁ =H	Tertiary R ₁₀ =R ₁₁ =CH ₃
Θ _{O3C1C2O4}	0.5 °	-2.5 °	-1.7 °
-E _{G3} (a.u)	230.383210	269.662606	308.946165 ^b
ΔH ^o _f (kcal/mol)	84.0	72.9	60.7
E _{act} (kcal/mol) ^a	0.3	3.1	4.2

^a Relative to M1. ^b Its E(Thermal) had been calculated from its MP2(FULL)/6-31G* value.

Figure 7: MP2 (FULL)/6-31G* Optimized key geometrical parameters, G3-enthalpy, ΔH^o_f and E_{act} values of OH//CH₃, OH//H and O//O rotational transition states.

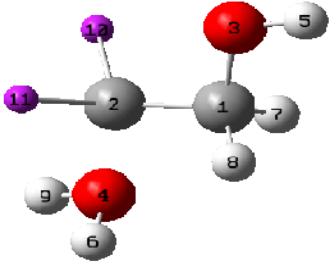
Here again, the value of the dihedral angle Θ_{O3C1C2R10} is larger than that of Θ_{O4C2C1H8} in OH//H TS (figure 7), although both OH and ⁺OH₂ are eclipsed with H. This observation confirms the importance of the number of the lone pairs of electrons on oxygen in determining its size. As the number of electron-pairs on oxygen increases, its size will increase.

O//O Transition states

The O//O eclipsed transition state is formed during the conversion of M1 to its mirror image in 1°, 2° and 3°. The small values of E_{act} are due to the existence of the intramolecular H-bonding in O//O transition state (figure 7). The values of the dihedral angles $\Theta_{O_3C_1C_2O_4}$ are ranging from 0.5° to 2.5° in the three transition states 1°, 2° and 3° (figure 7)

Anti Minima (M6) Formation

Anti minima (M6) are obtained from gauche minima through OH//CH₃ and/or OH//H transition states via rotation. The values of dihedral angle $\Theta_{O_3C_1C_2O_4}$ are 180.0°, 173.0° and



Parameters	Primary $R_{10}=R_{11}=H$	Secondary $R_{10}=H;$ $R_{11}=CH_3$	Tertiary $R_{10}=R_{11}=CH_3$
$r_{C_2-O_4}$	1.529Å	1.560Å	1.592Å
$\Theta_{O_3C_1C_2O_4}$	180.0°	173.0°	-178.2°
$-E_{G_3}$ (a.u)	230.364612	269.650681	308.935504
ΔH_f° (kcal/mol)	95.7	80.4	65.8
E_{rel} (kcal/mol) ^a	12.0	10.6	9.3

^a Relative to M1

Figure 8: MP2 (FULL)/6-31G* $r_{C_2-O_4}$ and OCCO dihedral angles, G3-enthalpy, ΔH_f° and E_{act} values of anti minima (M6).

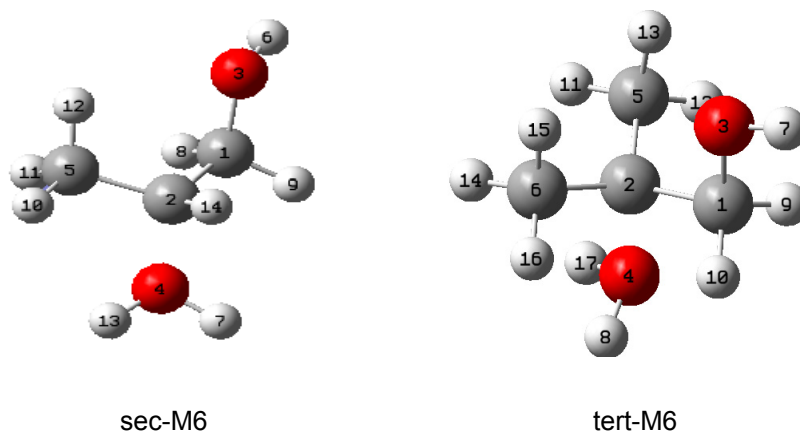


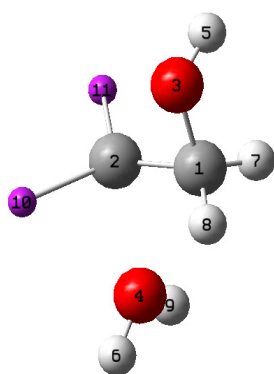
Figure 9: MP2 (FULL)/6-31G* Optimized structures of sec- and tert- anti minima (M6)

-178.2° in 1°, 2° and 3° species; respectively (figure 8). NBO analysis for sec-M6 (figure 9) species indicates that there is a significant HC between the anti bonds $\sigma_{C_5-H_{12}}$ and $\sigma^*_{C_2-O_4}$. The value of the dihedral angle $\Theta_{O_4C_2C_5H_{12}}$ is 176.4°. This HC increases the bond length of C₂-O₄. The bond lengths of C₂-O₄ are 1.529Å and 1.560Å in 1° and 2° species; respectively. Each methyl group in tert-M6 has an anti hydrogen to the protonated oxygen. The values of the dihedral angles $\Theta_{O_4C_2C_5H_{13}}$ and $\Theta_{O_4C_2C_6H_{15}}$

(figure 9) are -172.3° and 176.7° ; respectively. This anti configuration allows HC between σ_{C2-O4}^* molecular orbital and each of σ_{C5-H13} and σ_{C6-H15} bonds as shown in NBO analysis. Therefore, the r_{C2-O4} bond in 3° species (1.592\AA) is longer than that in 2° (1.560\AA) (figure 8).

HO-Bisected transition state ($TS_{6,7}$)

The formation of protonated epoxide, M7, from anti conformer, M6, requires passing through HO-bisected transition state, $TS_{6,7}$ (Figure 10). The PES for the two transition states which can be formed from the anti conformer are shown in figure 11. The rates of formation of the rotational transition states, OH//H and/ or OH//CH₃, are much faster than that of formation of HO-bisected transition state. This conclusion could be deduced by comparing the activation energy values of the formed transition states (figure 11). This indicates that anti converts more rapidly to gauche rather than to epoxide.

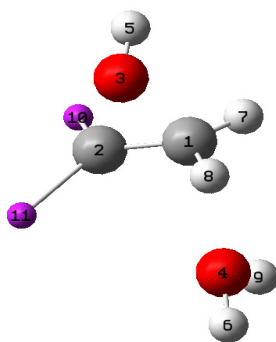


$TS_{6,7}$

HO-bisected transition states

Parameters	Primary $R_{10}=R_{11}=H$	Secondary $R_{10}=H;$ $R_{11}=CH_3$	Tertiary $R_{10}=R_{11}=CH_3$
$\Theta_{R_{10}C_2C_{10}O_3}$	82.8°	75.7°	84.2°
$\Theta_{R_{11}C_2C_{10}O_3}$	-76.6°	-85.6°	-81.6°
$-E_{G3}(\text{a.u.})$	230.347645	269.634028	308.923610
$\Delta H_f^\circ(\text{kcal/mol})$	106.3	90.8	73.3
$E_{act}(\text{kcal/mol})^a$	10.6	10.4	7.5

^a Relative to M6.



(M7)

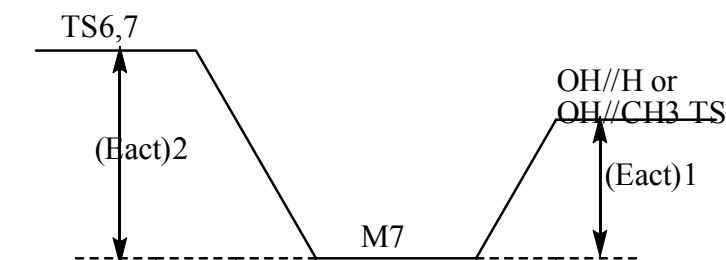
Hydrated protonated

Parameters	Primary $R_{10}=R_{11}=H$	Secondary $R_{10}=H;$ $R_{11}=CH_3$	Tertiary $R_{10}=R_{11}=CH_3$
r_{C1-O3}	1.533\AA	1.543\AA	1.536\AA
r_{C2-O3}	1.558\AA	1.569\AA	1.603\AA
$\theta_{O_3C_1C_2}$	63.0^\circ	63.2^\circ	64.8^\circ
$\theta_{O_3C_2C_1}$	61.3^\circ	61.3^\circ	60.2^\circ
$-E_{G3}(\text{a.u.})$	230.353409	269.640597	308.928082^b
$\Delta H_f^\circ(\text{kcal/mol})$	102.7	86.7	70.5
$E_{rel}(\text{kcal/mol})^c$	7.0	6.3	4.7

^b 3° epoxide does not exist at RHF. Therefore, its G3-enthalpy had been calculated step by step. See computational details epoxide minima section.

^c Relative to M6.

Figure 10: MP2(FULL)/6-31G* Optimized key geometrical parameters, G3-enthalpy, ΔH_f° and E_{rel} values of $TS_{6,7}$ and M7.



Species	$E_{act 2}$ (kcal/mol)	Species	$E_{act 1}$ (kcal/mol)
1°	10.6	OH//H (1°)	0.9
2°	10.4	(2°)	1.2
3°	7.5	OH//CH ₃ (2°)	2.7
		(3°)	2.5

Figure 11: PES for formation of the transition states which can be formed from anti conformer.

The optimized values of key geometrical parameters of HO-bisected transition state are shown in figure 10. It is formed by decreasing of $\theta_{O_3C_1C_2}$ angle and lengthening $r_{C_1-O_3}$ bond of anti conformer (figure 10). The values of dihedral angles $\Theta_{R_{10}C_2C_1O_3}$ and $\Theta_{R_{11}C_2C_1O_3}$ (figure 10) indicate that the 1°, 2° and 3° transition states have bisected structures.

Hydrated Protonated Epoxide Minima (M7)

The optimized values of key geometrical parameters of epoxides minima are shown in figure 10, the data indicate that $r_{C_2-O_3}$ bonds are longer than $r_{C_1-O_3}$ bonds in 1°, 2° and 3° epoxides. NBO analysis of 1° epoxide shows that there is HC between the pairs of electrons on O_4 and $\sigma^*_{C_2-O_3}$ molecular orbital. This HC causes the lengthening of $r_{C_2-O_3}$ bond. However, this type of HC is not found in 2° and 3° epoxides as shown by NBO analysis. The lengthening of $r_{C_2-O_3}$ bonds in 2° and 3° epoxides is caused by another type of HC.

The nucleophile usually attacks the more substituted carbons in asymmetrical protonated epoxides^[15], because it has more carboncation character^[26]. The positive charge is stabilized by methyl group(s) via HC. NBO analysis shows that the main HC is between $\sigma_{C_5-H_{10}}$ and $\sigma^*_{C_2-O_3}$ (sec-M7, figure 12), which increases the bond length of C_2-O_3 in 2° epoxide. H_{10} and O_3 are anti to each other and the value of dihedral $\Theta_{H_{10}C_5C_2O_3}$ is -165.9° .

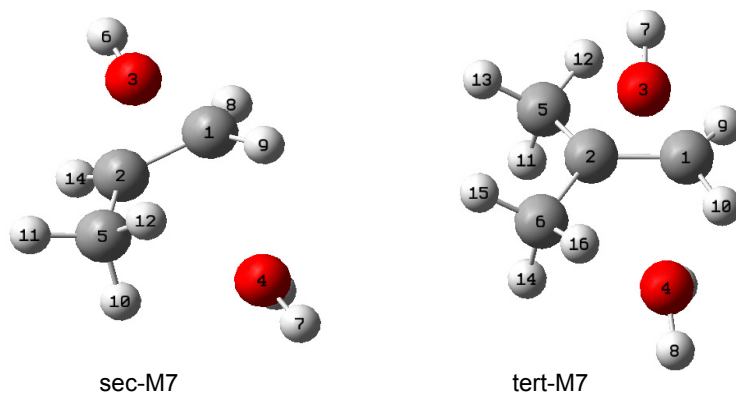


Figure 12: sec- and tert- M7 minima.

Figure 12 also indicates that H₁₁ and H₁₄ are anti to O₃ in tert-M7, and the values of dihedral angles $\Theta_{\text{H11C5C2O3}}$ and $\Theta_{\text{H14C6C2O3}}$ are 163.5° and -159.4°; respectively. From above data, it is expected that 3° epoxide has more effective HC. This HC exists between the anti-bonding molecular orbital $\sigma^*_{\text{C2-O3}}$ and each of the $\sigma_{\text{C5-H11}}$ and $\sigma_{\text{C6-H14}}$ bonds as it is confirmed by NBO analysis. This effective HC causes more lengthening of r_{C2-O3} bond in 3° epoxide.

Conclusion

The G3 calculations confirm that ethanediol, 1,2-propanediol and 2-methy-1,2-propanediol rearrange to aldehydes through concerted mechanism in the gas phase reactions. This is based on the fact that formation of carbocations as intermediates requires much higher activation energies than that required for the formation of H-bridged transition states in the concerted mechanisms. The G3 calculations give more confirmative conclusion, especially for 2-methy-1,2-propanediol than RHF calculations.

Epoxides can not be formed as byproducts or intermediates in the studied compounds. This result could be attributed to two reasons. First, carbocations are not formed as intermediates. Secondly, formation of anti conformer requires high activation energy. Even it is formed; the anti converts more rapidly to the gauche conformer rather than epoxide, since the activation energy for the formation of the epoxide is much higher.

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Appendix

Additional MP2 (FULL)/6-31G* Optimized key geometrical parameters for studied minima and transition states.

A) Gauche minima (M1)

Parameters	Primary R10=R11=H	Secondary R10=H; R11=CH3	Tertiary R10=R11=CH3
r_{C1-C2}	1.518Å	1.518Å	1.526Å
r_{C1-O3}	1.439Å	1.438Å	1.438Å
$\Theta_{O3C1C2O4}$	44.0°	44.5°	45.5°
$\Theta_{H8C1C2O4}$	162.8°	176.9°	165.0°

B) Gauche transition states (TS_{1,2})

Parameters	Secondary R10=H;R11=CH ₃	Tertiary R10=R11= CH ₃
r_{C1-C2}	1.531	1.538
r_{C1-O3}	1.476	1.484
r_{C2-O4}	1.481	1.484

C) Gauche minima (M2)

Parameters	Secondary R10=H;R11=CH ₃	Tertiary R10=R11= CH ₃
r_{C1-C2}	1.522 Å	1.533 Å
r_{C2-O4}	1.452 Å	1.467 Å
$\Theta_{O3C2C1O4}$	42.5°	40.8°

D) H-Bridged transition states (TS_{1,3})

Parameters	Primary R10=R11=H	Secondary R10=H; R11=CH ₃	Tertiary R10=R11= CH ₃
r_{C1-C2}	1.398Å	1.401Å	1.403Å
r_{C1-H8}	1.233Å	1.213Å	1.226Å
r_{C2-H8}	1.498Å	1.543Å	1.513Å

E) Hydrated protonated aldehyde minima (M3)

Parameters	Primary R10=R11=H	Secondary R10=H; R11=CH3	Tertiary R10=R11=CH3
r_{C1-O4}	1.769Å	2.272Å	2.296Å
$\Theta_{H8C2C1H7}$	70.4°	84.9°	78.4°

F) H-Bridged transition states (TS_{4,5})

Parameters	Secondary	Tertiary
	R7=H;R8=CH ₃	R7=R8=CH ₃
r _{C1-C2}	1.426Å	1.414Å
r _{C2-O3}	1.374Å	1.357Å
r _{C1-H5}	1.819Å	1.582Å
r _{C2-H5}	1.152Å	1.200Å
∠ _{O3C2C1R7}	173.9°	-169.1°
∠ _{O3C2C1R8}	-9.1°	11.3°

G) Protonated aldehyde minima (M5)

Parameters	Primary	Secondary	Tertiary
	R7=R8=H	R7=H; R8=CH ₃	R7=R8=CH ₃
r _{C1-C2}	1.452 Å	1.453 Å	1.449 Å
r _{C2-O3}	1.270 Å	1.272 Å	1.275 Å
r _{O3-H6}	0.990 Å	0.989 Å	0.988 Å
∠ _{O3C2C1H5}	-123.0°	126.1°	138.8°
∠ _{H4C2C1H5}	57.0°	-53.9°	-44.6°
∠ _{H4C2C1R8}	-179.9	-180.0	-169.2

H) OH//CH₃ TS

Parameters	Secondary	Tertiary
	R ₁₀ =H; R ₁₁ =CH ₃	R ₁₀ =R ₁₁ =CH ₃
r _{C1-C2}	1.533 Å	1.538 Å
r _{C1-O3}	1.410 Å	1.412 Å
r _{C2-O4}	1.576 Å	1.607 Å
r _{C2-C5}	1.499 Å	1.504 Å

I) OH//H TS

Parameters	Primary	Secondary
	R ₁₀ =R ₁₁ =H	R ₁₀ =H; R ₁₁ =CH ₃
r _{C1-C2}	1.524 Å	1.524 Å
r _{C1-O3}	1.411 Å	1.413 Å
r _{C2-O4}	1.533 Å	1.567 Å

J) O//O TS

Parameters	Primary	Secondary	Tertiary
	R ₁₀ =R ₁₁ =H	R ₁₀ =CH ₃ ; R ₁₁ =H	R ₁₀ =R ₁₁ =CH ₃
r _{C1-C2}	1.556 Å	1.557 Å	1.563 Å
r _{C1-O3}	1.448 Å	1.442 Å	1.445 Å
r _{C2-O4}	1.489 Å	1.514 Å	1.532 Å
r _{O3-H6}	1.428 Å	1.480 Å	1.481 Å
r _{O4-H6}	1.081 Å	1.056 Å	1.055 Å

K) Anti minima (M6)

Parameters	Primary	Secondary	Tertiary
	R ₁₀ =R ₁₁ =H	R ₁₀ =H; R ₁₁ =CH ₃	R ₁₀ =R ₁₁ =CH ₃
r _{C1-C2}	1.515Å	1.517Å	1.523Å
r _{C1-O3}	1.409Å	1.412Å	1.413Å
θ _{O3C1C2}	100.6°	101.8°	103.1°

L) HO-bisected transition states (TS_{6,7})

Parameters	Primary	Secondary	Tertiary
	R ₁₀ =R ₁₁ =H	R ₁₀ =H; R ₁₁ = CH ₃	R ₁₀ =R ₁₁ =CH ₃
r _{C1-C2}	1.457Å	1.459Å	1.470Å
r _{C1-O3}	1.468Å	1.462Å	1.453Å
r _{C2-O3}	1.837Å	1.920Å	2.012Å
θ _{O3C1C2}	77.8°	82.2°	87.0°
θ _{O3C2C1}	51.4°	49.0°	46.2°

M) Hydrated protonated epoxide minima (M7)

Parameters	Primary	Secondary	Tertiary
	R ₁₀ =R ₁₁ =H	R ₁₀ =H; R ₁₁ = CH ₃	R ₁₀ =R ₁₁ =CH ₃
r _{C1-C2}	1.445Å	1.448Å	1.451Å
r _{C1-O4}	2.549Å	2.625Å	2.655Å
r _{C2-O4}	2.900Å	2.869Å	2.881Å