



A DENSITY FUNCTIONAL STUDY OF REARRANGEMENT REACTION OF 2, 3-EPOXYPROPOXIDE ANION : PAYNE REARRANGEMENT

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Abstract: Density function study is used to study the rearrangement of 2,3-epoxypropoxide anion. 2,3-epoxypropoxide anion arrangement also known as Payne rearrangement which involves epoxide ring to open the initial three membered ring and rearrange to form new ring (path I) and also involves alternate path of which proceed through a four membered oxetane system(path II) . The energy barrier 11.8 Kcal mol⁻¹ is predicted for the path I is lesser as compared to 32.6 kcalmol⁻¹ predicted for path II . This shows that path I is more preferred over the path (II). This reaction is found to be exothermic in nature. All calculated values of geometries, activation energy are in good agreement with other post SCF method.

Keywords: Density Functional Theory, B3LYP and B3PW91 functional, 6-31 G(d) basis set, Payne rearrangement, 2,3-epoxypropoxide anion, exothermicity.

I. Introduction

The Payne rearrangement involves the cyclisation of alkoxide center at the more substituted carbon of the epoxide ring to open the initial three membered ring and form a new one (path I). Payne rearrangement can alternatively proceed through a four membered oxetane system (path II) Fig. 1. This rearrangement is reviewed experimentally (Payne,1962, Toshiro, 1998,1995). Theoretical studies (Hevko,1999, Dua,1997, Vilotijevic,2007, Bouyacoub,2002) have also been made for Payne- rearrangement. Density functional theory is the popular tool used here as its ability to include exchange and correlation functional at moderate cost in comparison to post SCF method for calculating the ground state properties of molecules. In this paper, we present the results of our Density Functional study of the rearrangement of 2,3-epoxypropoxide anion.

II. Methods of Calculation

In the present work, the calculations were carried out by ab-initio (Hehre, 1986) and density functional method (Parr,1989, Seminario,1991). Here B3LYP and B3PW91 density functional with 6-31 G(d) basis set used here for all calculations. The hybrid functional B3LYP used here has Becke's exchange functional correction (Becke, 1993,1988) and the gradient corrected correlation functional of Lee, Yang and Parr (Lee, 1988) and B3PW91 hybrid functional has Becke's exchange functional correction with Perdew and Wang's correlational functional (Perdew, 1992). Geometries optimization was made using analytical first derivatives. B3LYP function predicts the activation energy barrier for a number of reactions (Fan et al.,1990,Quin et.al.,1995,Kaushik et al.,1996,1997,Tandon et al.,1997, Rani et al.,1998,2000, Nazarpavar et al.

,2012, Miller et al. ,2014, Heidri, 2016, Chaoyue,2021, Parashar, 2021, Parashar et al. 2021). Gaussian 94 Quantum chemistry package (Frisch et al. 1995) was used for all calculations presented here. Results of other studies are also listed for comparison.

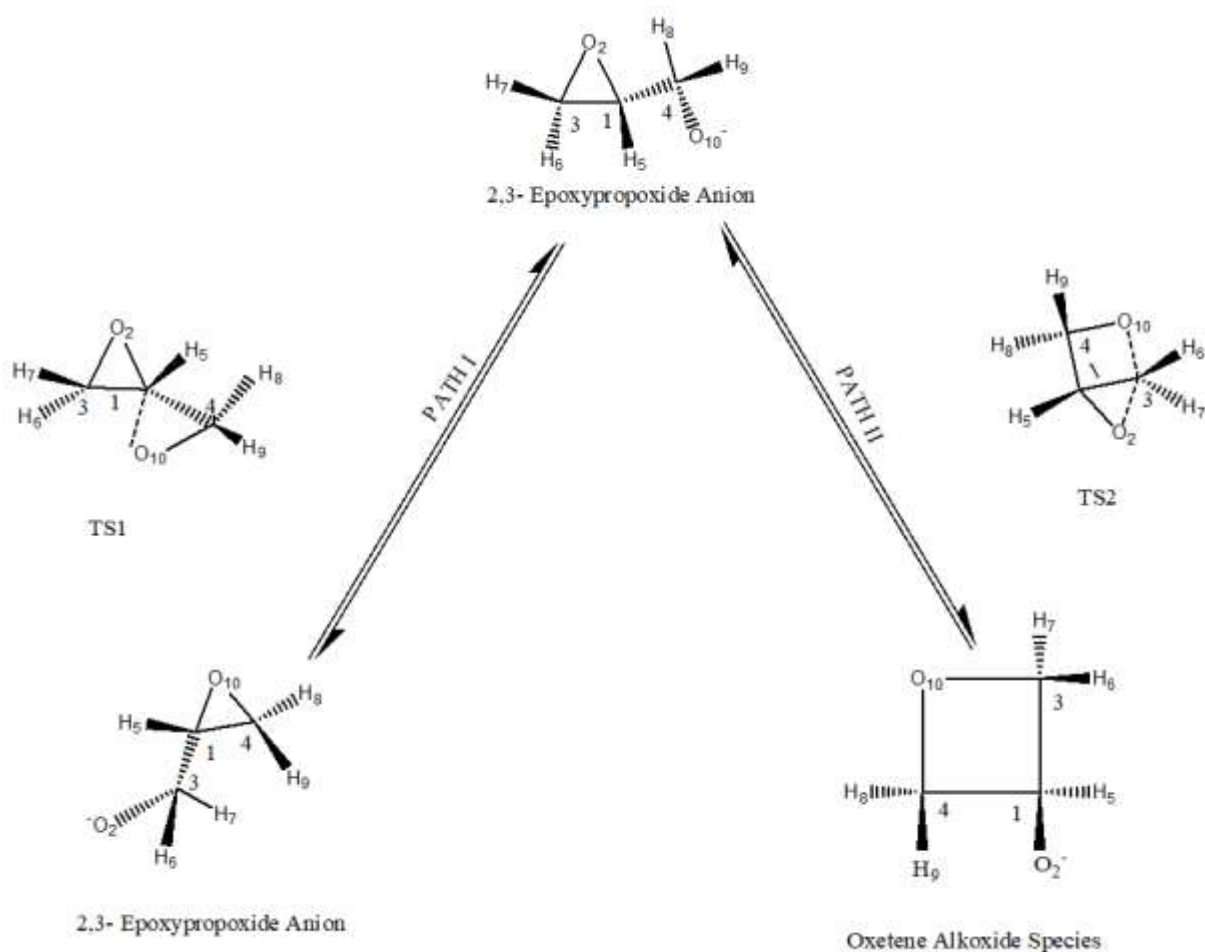


Fig .1: Rearrangement reaction of 2, 3-epoxypropoxide anion

III. Result and Discussion

The RHF/3-21G, RHF/6-31 G(d) , B3LYP/6-31 G(d) optimized geometries of 2,3 epoxypropoxide anion,TS1, TS2 and oxetane are listed in tables 1 to 4 . The optimized geometries using (B3LYP functional and 6-31G(d) basis set shows that for path I, O2-C1 distance increases and O10-C4-C1 angle decreases as one goes from the reactant to three membered transition state which is in good agreement with RHF method using 3-21G and 6-31G(d) basis set.

Similarly for path (II) there is a decrease in angle O10-C4-C1 using B3LYP (6-31G(d) functional which is again in good agreement with RHF method using 3-21G and 6-31G(d) basis set. RHF/3-21G optimized geometries are used to carry out the single point energy.

Table 1 : Calculated optimized geometries of the 2,3-epoxypropoxide anion

Parameters ^b	RHF/3-21G	RHF/6-31G(d)	B3LYP/6-31G(d)
Lengths			
O2-C1	1.491	1.432	1.475
C3-C1	1.466	1.448	1.464
C4-C1	1.534	1.532	1.546

H5-C1	1.073	1.081	1.095
H6-C3	1.075	1.082	1.097
H7-C3	1.073	1.080	1.095
H8-C4	1.120	1.124	1.151
H9-C4	1.120	1.124	1.152
O10-C4	1.357	1.317	1.319

Angles

C3-C1-O2	59.9	58.5	58.3
C4-C1-O2	119.6	120.7	122.4
H5-C1-O2	113.4	112.8	112.8
H6-C3-C1	120.6	121.3	121.4
H7-C3-C1	118.2	119.2	118.4
H8-C4-C1	103.7	104.7	103.7
H9-C4-C1	104.3	104.6	104.4
O10-C4-C1	110.1	111.1	110.6

Dihedral Angles

C4-C1-O2-C3	-111.2	-112.8	-111.2
H5-C1-O2-C3	109.2	108.3	108.2
H6-C3-C1-O2	103.1	102.8	103.7
H7-C3-C1-H6	152.4	153.1	151.2
H8-C4-C1-O2	39.3	41.3	40.2
H9-C4-C1-H8	-106.5	-107.3	-105.7
O10-C4-C1-H8	127.1	126.8	127.3

a. See Fig. 1

b. All bond lengths in Å and angles in degrees.

Table 2 : Calculated optimized geometries of the transition state^a (TS1) for reaction path (I)

Parameters ^b	RHF/3-21G	RHF/6-31G(d)	B3LYP/6-31G(d)
Lengths			
O2-C1	1.875	1.896	1.942
C3-C1	1.455	1.455	1.468
C4-C1	1.455	1.455	1.468
H5-C1	1.062	1.066	1.082
H6-C3	1.089	1.099	1.119
H7-C3	1.088	1.098	1.117
H8-C4	1.088	1.098	1.117

H9-C4	1.089	1.099	1.119
O10-C4	1.435	1.357	1.371
Angles			
C3-C1-O2	49.1	45.5	44.8
C4-C1-O2	120.3	122.8	123.3
H5-C1-O2	99.1	100.2	100
H6-C3-C1	116.1	115.8	115.8
H7-C3-C1	114.4	114.1	113.3
H8-C4-C1	114.4	114.1	113.2
H9-C4-C1	116.1	115.8	115.8
O10-C4-C1	80.9	84.7	86.3
Dihedral Angles			
C4-C1-O2-C3	-109.8	-109.3	-107.9
H5-C1-O2-C3	119.7	118.7	119.4
H6-C3-C1-O2	115.6	117.1	118.2
H7-C3-C1-H6	128.6	125.7	123.6
H8-C4-C1-O2	45.7	41.9	41
H9-C4-C1-H8	-128.6	-125.7	-123.5
O10-C4-C1-H8	115.8	117.2	118.2

a. See Fig. 1

b. All bond lengths in Å and angles in degrees.

Table 3 : Calculated optimized geometries of the transition state^a (TS2) for reaction path (II)

Parameters ^b	RHF/3-21G	RHF/6-31G(d)	B3LYP/6-31G(d)
Lengths			
O2-C1	1.421	1.352	1.364
C3-C1	1.437	1.437	1.456
C4-C1	1.562	1.550	1.571
H5-C1	1.090	1.100	1.118
H6-C3	1.061	1.065	1.082
H7-C3	1.073	1.078	1.093
H8-C4	1.098	1.108	1.126
H9-C4	1.096	1.103	1.119
O10-C4	1.424	1.365	1.37
Angles			

C3-C1-C4	96.7	96.3	97.8
C4-C1-O2	131.3	130.1	128.9
H5-C1-C4	109.1	108.2	107
H6-C3-C1	116.3	116.3	116.3
H7-C3-C1	123.5	123.9	122.6
H8-C4-C1	108.9	109	107.9
H9-C4-C1	112.4	112.8	118.8
O10-C4-C1	97.5	100.1	101.4

Dihedral Angles

O2-C1-C4-H5	-154	-148.8	-145.3
C3-C1-C4-H5	118.5	117.1	116.7
H6-C3-C1-C4	59.6	59.6	58.2
H7-C3-C1-H6	162.6	160	153.5
H8-C2-C1-H6	118.7	117.3	115.9
H9-C4-C1-H5	33.1	37.7	40
O10-C4-C1-H9	-121.1	-121.9	-122

a. See Fig. 1

b. All bond lengths in Å and angles in degrees.

Table 4 : Calculated optimized geometries of the oxetane alkoxide species

Parameters ^b	RHF/3-21G	RHF/6-31G(d)	B3LYP/6-31G(d)
Lengths			
O2-C1	1.309	1.295	1.294
C3-C1	1.623	1.575	1.610
C4-C1	1.118	1.575	1.610
H5-C1	1.084	1.123	1.149
H6-C3	1.085	1.09	1.105
H7-C3	1.084	1.091	1.106
H8-C4	1.084	1.09	1.105
H9-C4	1.085	1.091	1.106
O10-C4	1.474	1.426	1.448
Angles			
H5-C1-O2	117.4	116.1	117.4
C3-C1-H5	102.3	104.8	103.5
H5-C1-C4	102.3	104.8	103.5

H6-C3-C1	110.4	111.4	110.6
H7-C3-C1	119	120.3	120.8
H8-C4-C1	110.4	111.4	110.6
H9-C4-C1	119	120.3	120.8
O10-C4-C1	91.5	91.9	92.3

Dihedral Angles

C3-C1-H5-O2	138	137.8	138.4
C4-C1-H5-O2	-138	-137.8	-138.4
H6-C3-C1-H5	-159.2	-156.8	-157.5
H7-C3-C1-H6	130.4	129.7	129.4
H8-C4-C1-O10	-113.4	-113.8	-114.1
H9-C4-C1-O10	116.2	116.5	116.6
O10-C4-C1-H5	-87.4	-89.4	-88.5

- a. See Fig. 1
 b. All bond lengths in Å and angles in degrees.

Relative energies of rearrangement via path I and path II are given in Table 5. The difference in energy of TS1 and reactant compared to difference in energy of TS2 and reactant shows that a three membered transition state is preferred over the four membered transition state. This barrier height is further reduced by inclusion of correlational functional. ΔE values show that reaction is exothermic in nature. B3LYP/6-31 G(d) // RHF/3-21G results are very similar to B3PW91/6-31 G(d) //RHF/3-21G results shown in Table 5. These are very close to the results of full optimization using B3LYP density functional and 6-31G(d) basis set. Our calculated energy barrier and ΔE result are in good agreement with the result of high quality quantum chemical studies (Dua et al.1997).

Table 5 : Relative energies of reactants, TS and product (kcal mol⁻¹) for the rearrangement reaction of 2,3-epoxypropoxide anion

		Relative Energies ^a				
		A	B	C	D	Other ^b
Path(I)	E_a	20.6	9.0	11.2	11.8	10.8
Path(II)	E_a	48.1	29.3	31.7	32.6	29.2
ΔE		-9.0	-8.6	-9.2	-9.1	-6.5

- a) E_a is the energy of activation and ΔE is the difference in energy of product and reactant and E_a is energy of activation energy. Values are obtained after zero point vibrational energy correction.
 b) Obtained from reference (Dua 1997)

- A RHF/6-31G(d)
 B RB3LYP/6-31G(d)
 C RB3LYP/6-31G(d)//RHF/3-21G
 D RB3PW91/6-31G(d)//RHF/3-21G

IV. Conclusions

1. DFT method using B3LYP and B3PW91 using 6-31G(d) basis set give reliable geometry which are comparable to those obtained of high quality quantum chemical calculations.
2. For Payne rearrangement the two path are predicted in which path I is preferred over path II.
3. Both paths I and II are predicted to be exothermic in nature.

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