

## Photodissociation Mechanism Study of 1, 3-Dibromopropane using Theoretical Calculations\*

Received : 7/12/2017

Accepted : 18/1/2018

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### **Abstract:**

A simulation study has been conducted by using Quantum calculation methods like DFT, *Ab-initio* and semiempirical methods to estimate the photolysis mechanism for 1,3-dibromopropane in the gas phase and its effect on the ozone layer.

Energetic properties have been calculated like total energy and thermodynamic functions ( $G$ ,  $S$ ,  $H_f$ ) for all chemical species that's participate in the suggested reaction mechanism. Geometry optimized and single point calculation has been done to understand the configuration interaction singly excited state for three different conformations of 1, 3-dibromopropane which is found that the  $C_2$  isomer is the most stable with total energy being equal to  $-26652.031 \text{ kCal mol}^{-1}$ . Molecular orbital and their energy gap has been calculated using *Ab initio*//6-311G\* and Beck 88 LYP//3-21G(d) level.

The cleavage occurs at a wavelength equal to 442.571 nm and yields the 3-bromopropyl and bromine radical with activation energy equal to  $98.624 \text{ kCal mol}^{-1}$  calculated by using MNDO/d method. The 3-bromopropyl radical undergoing secondary dissociation through second C-Br bond to give the cyclopropane molecule as a final product with an energy barrier equal to  $68.83 \text{ kCal mol}^{-1}$ .

**Key words:** 1,3-dibromopropane, Ozone Depletion, Photolysis mechanism, transition state, Calculation methods.

### **Introduction:**

The depletion of the ozone layer, which was discovered 40 years ago that's resulted from compounds released to the atmosphere in the course of various industrial or technological human activities such as chlorofluorocarbons (CFC) and halons, has been of great environmental interest and has attracted numerous experimental and theoretical studies [1]. The concentration of ozone in the atmosphere is decreasing and large holes are being formed near the poles.

These changes are directly attributed to anthropogenic halogens compounds with chlorine, bromine and iodine have the most potential for atmospheric ozone depletion.[2] Hydrochlorofluorocarbons (HCFC) are chemical compounds that have been identified as a replacement to CFC and halon compounds which have a shorter atmospheric lifetime and less ozone depletion potential due to oxidation by hydroxyl(OH) radical. These compounds undergo photolysis releasing

the halogens that participate in the ozone depletion cycles. Bromine radical which contributes in catalytic ozone destruction is 40–50 times more effective than Cl at depleting ozone [3-5].

Brominated hydrocarbons can have a significant impact on the degradation of stratospheric ozone due to bromine radical reactivity in ozone depletion cycle compared with chlorine radical [6]. Brominated hydrocarbons are very short-lived compounds that's suggested as replacements for chlorofluorocarbons in according to the Montreal Protocol on substances that deplete the ozone layer. When these compounds transported and photolyzed in the stratosphere, can produce Br atoms that participate in ozone destruction cycle an important example of these compounds is bromopropane. Bromopropane has been used as the active component of industrial cleaning solvents where under UV-radiation undergoing photoreaction consists of excitation of nonbonding  $p$  electron of bromine directly to the lowest energy available anti-bonding molecular orbital followed by a quick dissociation, which involving  $n \rightarrow \sigma^*$  electronic excitation localized on the C–Br bond [7-10].

1,3-Dibromopropane is a colorless to light brown liquid which is a very important

compound to form  $C_3$ -bridged compounds such as cyclopropane by using sodium as a catalyst that's proposed by Freund in 1881. 1,3-dibromopropane present in three conformations with respect to the rotation along the C-C bonds, these are the anti-anti, anti-gauche and the gauche-gauche conformation and there is a conformational equilibrium between these isomers [11-12].

The present study tends to investigate the photolysis net equation for 1,3-dibromopropane under the influence of UV-radiation and geometry optimized determination of the species result in photolysis reactions and its interaction with ozone in the stratospheric layer by using quantum computational methods such as semiempirical, *Ab initio*/HF and DFT/ Beck 88 LYP also, vibration analysis has been predicted to estimate the zero point energy and stationary points on the potential energy surface. Transition state searching has been done by using synchronous transit method with a quadratic option to evaluate the activation energy of the reactions and the most probable pathway [13-15].

### **Computational Details:**

All quantum mechanics calculations are done using the Hyperchem 8.02 program package. Geometries were calculated using the HF and DFT with Beck 88 exchange potential and LYP correlation potential with implemented of 3-21G(d) basis set. Single point energies have been calculated to estimate the total energy and electrostatic properties for all ground-state

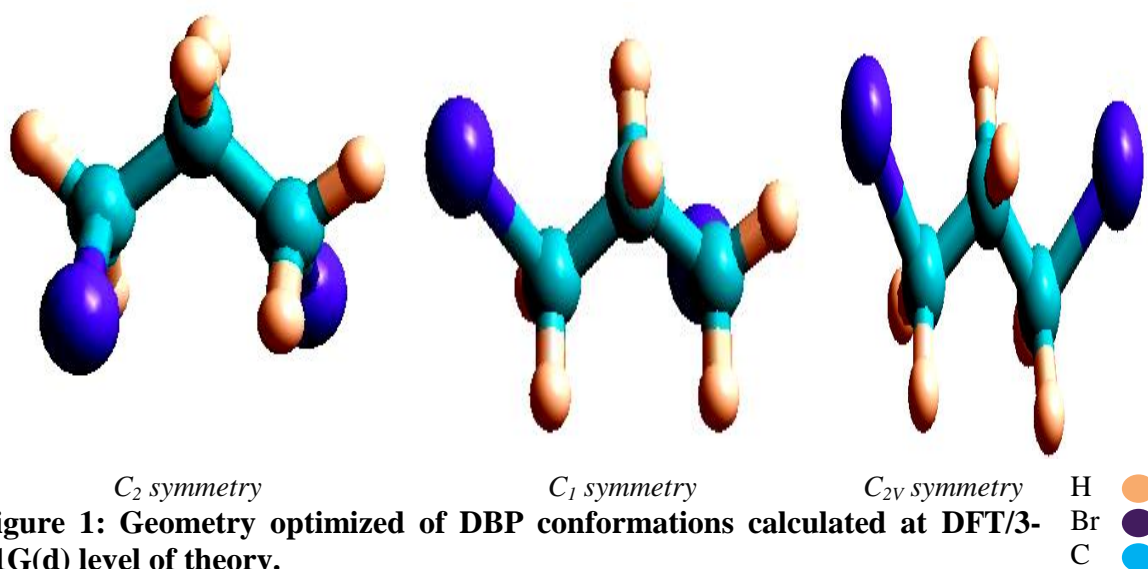
species. Potential energy surface of bond stability had been performed at PM3/ Configuration Interaction/Singly Excited (4\*4) level of theory to the bond length, bond angle of 1, 3-dibromopropane and molecular orbital energies (HOMO and LUMO) with energy gap have been computed by Austin Model 1 method [16 - 18].

## RESULTS AND DISCUSSION:

### Optimizing structure of 1,3-Dibromopropane conformations:

1,3-Dibromopropane compound has been optimized under different quantum computational methods in three different conformations with respect to the rotation along the C-C bonds as given in Fig.1. The energetic properties of these three

conformations have been calculated using the PM3 method as represented in Table 1. The anti-anti conformation takes  $C_{2v}$  symmetry, gauche-gauche with  $C_2$  symmetry and the last conformation gauche-anti with  $C_1$  symmetry.



**Table 1: Energetic properties of DBP conformations calculated at PM3 method, energy values in  $\text{kCal mol}^{-1}$  unit.**

Type of calculations	<i>symmetry</i>		
	gauche-gauche	gauche-anti	anti-anti
	$C_2$	$C_1$	$C_{2v}$
Total energy	-26652.03096	-26651.6711	-26651.4958
Binding energy	-888.1	-887.7374	-887.562
Heat of formation	-9.4993	-9.147	-8.9794
Dipole moment D	1.626	1.803	1.823
ZPE	52.8288	52.611	52.531
HOMO eV	-11.0655	-11.09445	-11.0928
LUMO eV	-0.35	-0.4367	-0.5665
$E_g$ eV	10.7155	10.6578	10.526

They found the relative stabilities of 1,3-dibromopropane have been reported as 67% GG, 30% AG and 3% AA, where  $C_2$  symmetry conformation is the more stable isomer than other isomers of DBP, which proved with the lowest value of the total energy compared with recent studies [19-21]. The geometry optimization of gauche-

gauche conformation also, has been computed by using other semiempirical methods such as AM1, MNDO/d and *Ab initio*, DFT methods as shown in Table 2. The energy gap calculation gives high value with *Ab initio* method compared with semiempirical, which equal to 14.691 eV.

**Table 2: DBP energy values computed with different methods in kCal mol<sup>-1</sup> unit.**

Type of calculation	Semiempirical		<i>Ab initio</i>	DFT
	AM1	MNDO/d	6-311G*	3-21G(d)
Total energy	-27078.02	-22298.394	-3301874.961	-3288853.863
Binding energy	-893.359	-872.395	-	-
Heat of formation	-15.733	6.366	-	-
Dipole moment D	1.621	1.862	2.531	2.338
ZPE	53.1	56.1	57.563	36.206
HOMO eV	-10.727	-10.453	-11.198	-6.417
LUMO eV	0.622	0.443	3.493	-1.346
E <sub>g</sub> eV	11.349	10.896	14.691	7.763

#### Investigation of 1,3-Dibromopropane bonds reactivity :

Chemical reactivity of 1,3-Dibromopropane is achieved by comparing the bond stability of real molecular structure. Table 3 represented the bond parameters, bond length and bond angles were computed by a PM3

method. The values of C-Br,  $C_1$ - $C_2$  bond length also,  $C_1$ - $C_2$ - $C_3$  angle reached the values computed by the DFT method in recent studies[12].

**Table 3: Bonds parameters of DBP conformations computed at PM3 method.**

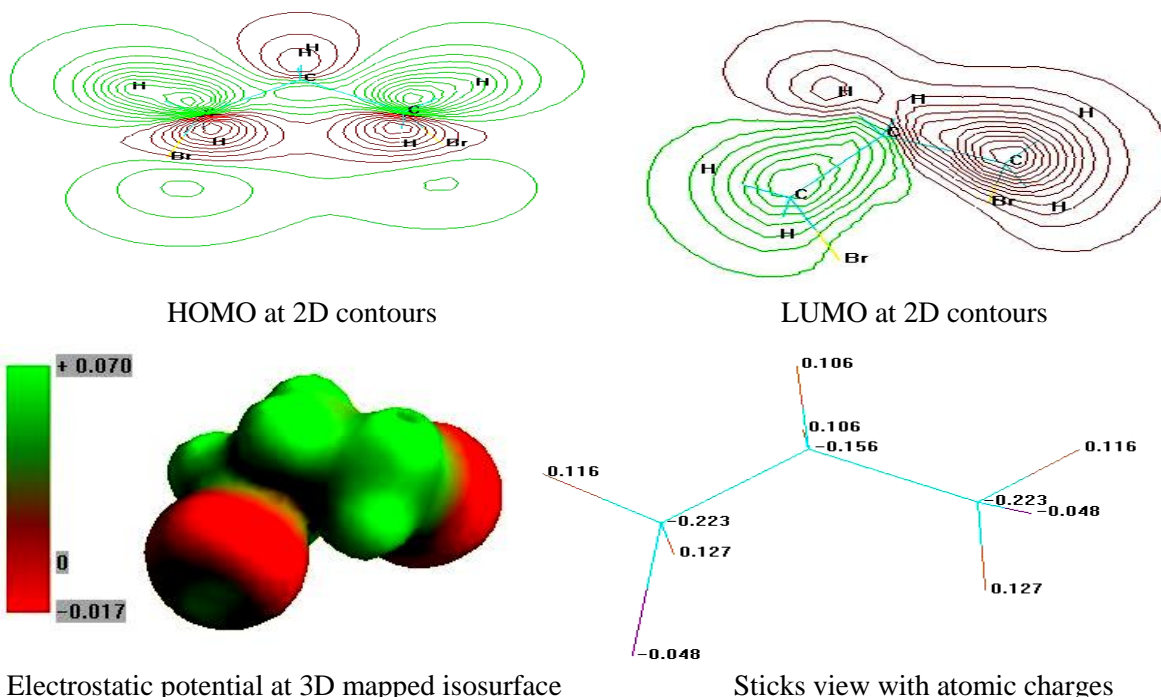
Bonds	Bond length (Å)			Bond angle(Degree)		
	$C_2$ symmetry	$C_1$ symmetry	$C_{2v}$ symmetry	$C_2$ symmetry	$C_1$ symmetry	$C_{2v}$ symmetry
$C_2$ - $C_3$	1.499	1.497	1.5	-	-	-
$C_1$ -Br <sub>4</sub>	1.959	1.952	1.952	-	-	-
$C_1$ -H <sub>5</sub>	1.1	1.102	1.101	-	-	-
$C_1$ - $C_2$	1.499	1.5	1.5	-	-	-
$C_2$ -H <sub>8</sub>	1.1097	1.1092	1.109	-	-	-
$C_3$ -H <sub>9</sub>	1.102	1.1	1.1	-	-	-
$C_1$ -Br <sub>4</sub> -H <sub>5</sub>	-	-	-	107.348	108.17	107.837
$C_2$ -H <sub>7</sub> - $C_1$	-	-	-	109.544	109.606	109.913
$C_1$ - $C_2$ - $C_3$	-	-	-	112.554	112.01	111.552
$C_2$ - $C_3$ -H <sub>7</sub>	-	-	-	109.513	109.873	109.953

The physical properties of 1,3-dibromopropane have been calculated with

semiempirical AM1 method as represented in Fig 2. The electrostatic potential at three

dimension mapped isosurface showed with red and green color, where the red color centered on the bromine atom which

represented the negative charge density while green color is a positive charge density [22].



**Figure 2: Physical properties of DBP computed at semiempirical AM1 method.**

The potential energy stability has been used to predict the bond length, bond angle reactivity of 1,3-dibromopropane molecule and finding the most probable bond in photolysis reaction. Energetic

values of main bonds in 1,3-DBP molecule have been calculated by using PM3/CI(4\*4) method as given in Table 4 and Fig. 3 [17].

**Table 4: Potential energy stability search of bonds length computed at PM3/ CI(4\*4) in kCal mol<sup>-1</sup> unit.**

Type of bonds	Equilibrium energy	Equilibrium length Å	Breaking energy	Dissociation energy	Wavelength nm
C <sub>1</sub> -Br <sub>4</sub>	-888.1	1.959	-823.712	64.39	442.571
C <sub>1</sub> -H <sub>6</sub>	-888.097	1.102	-776.527	111.57	256.52
C <sub>1</sub> -C <sub>2</sub>	-888.097	1.499	-785.527	102.57	279.01
C <sub>2</sub> -C <sub>3</sub>	-888.097	1.499	-785.516	102.582	278.977
C <sub>2</sub> -H <sub>8</sub>	-888.097	1.11	-788.709	99.389	287.939
C <sub>3</sub> -H <sub>10</sub>	-888.096	1.102	-779.585	108.51	263.736
C <sub>1</sub> -H <sub>5</sub>	-888.0973	1.1	-779.531	108.566	263.6

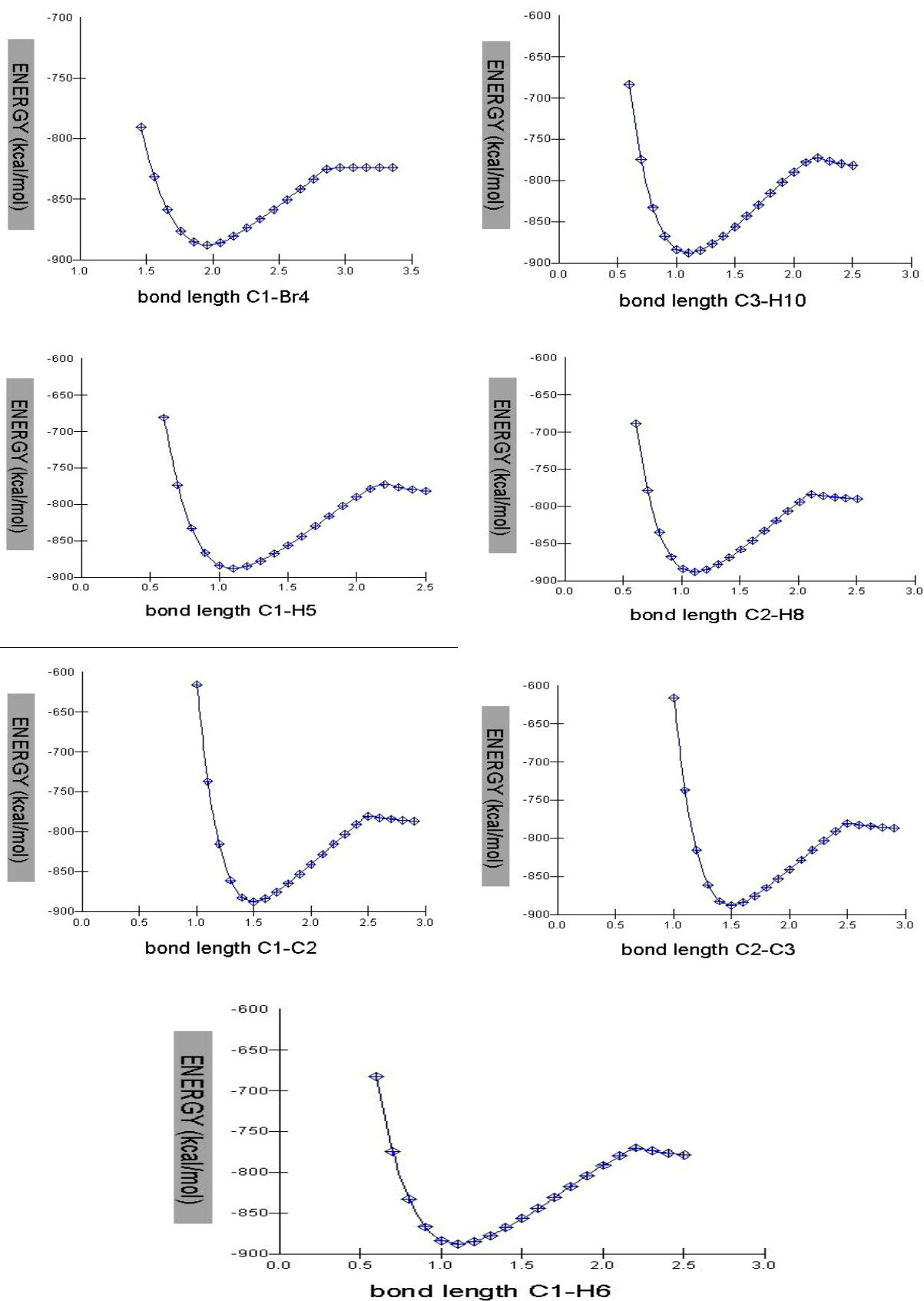


Figure 3: Potential energy surface of 1,3-DBP computed at PM3/CI (4\*4) method.

These values predict that C-Br bond is less stable than C-H and C-C bonds toward photolysis due to its bond length equal to 1.959 Å, and it is required less energy to be a breakdown, also it is required less value of dissociation energy which equal to

64.39 kCal mol<sup>-1</sup>, with a wavelength value 442.571 nm where the breakdown of C-Br bond occurs in the visible region. The dissociation energy of C-C and C-H agreed with recent experimental and theoretical studies [7], [23].

#### **Photolysis pathways of 1,3-DBP:**

The first photodissociation path is the breakdown of C-Br bond with a dissociation energy and wavelength equal to 64.39 kCal mol<sup>-1</sup>, 442.571 nm respectively. The 3-bromopropene radical which is the main molecule in photodissociation pathways is the product of this path. The potential energy surface has been computed for this molecule to

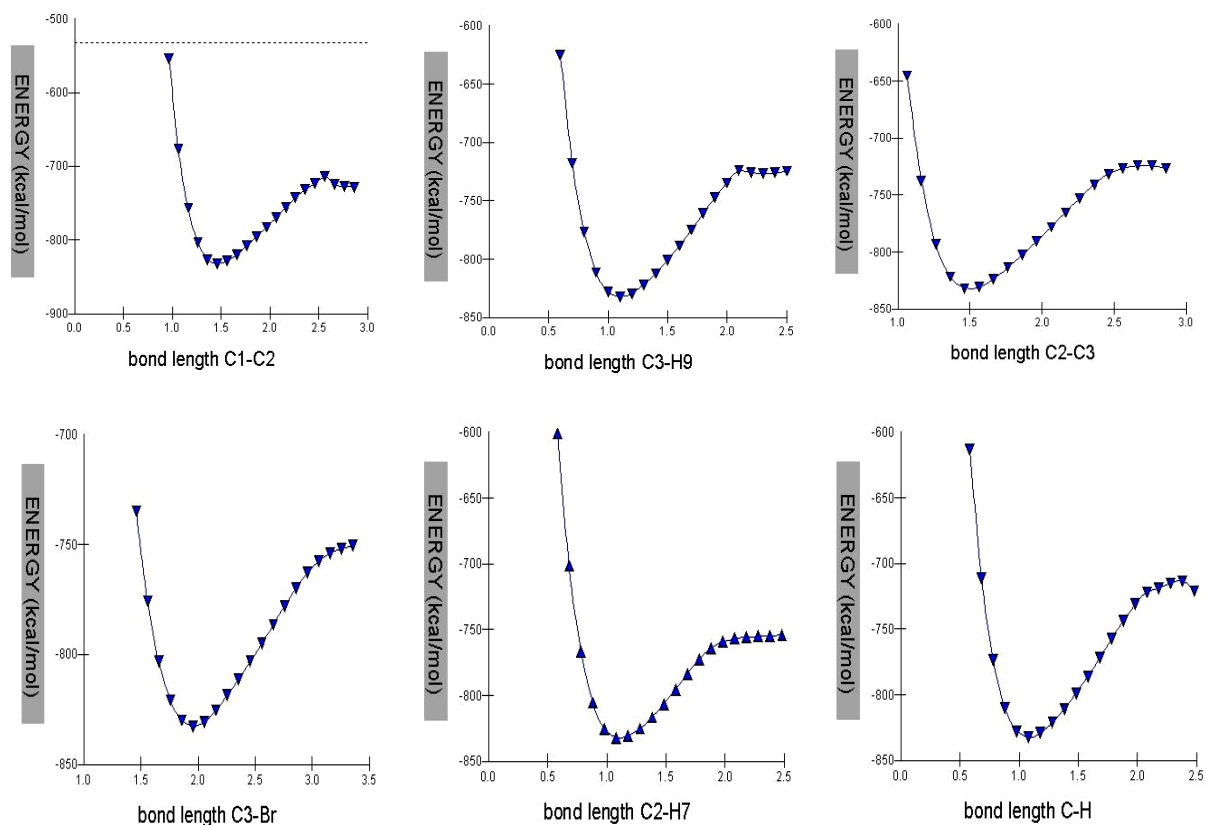
predict the most reactive bond as shows in Table 5 and Fig.4. The potential energy surface calculation of 3-bromopropene radical shows that three types of bonds will undergo photodissociation C<sub>2</sub>-H<sub>7</sub>, C<sub>3</sub>-Br and C<sub>2</sub>-C<sub>3</sub> to give us a different fragment that contribute to ozone depletion.

**Table 5 : Potential energy surface of bond length for 3-bromopropene radical computed at PM3/CI(4\*4) method in kCal mol<sup>-1</sup> unit.**

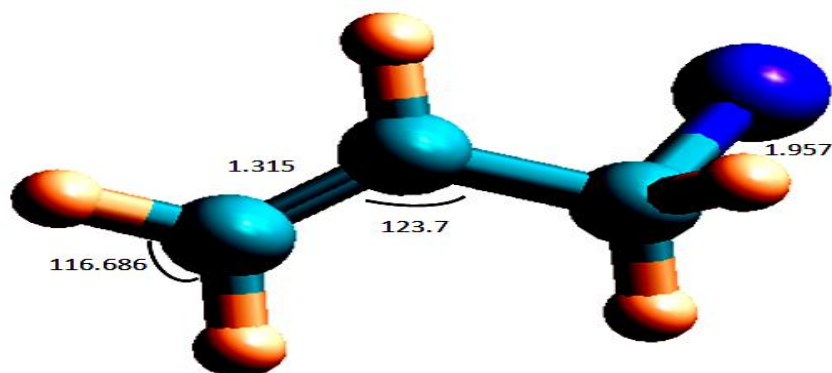
Type of bonds	Equilibrium energy	Equilibrium length Å	Breaking energy	Dissociation energy
C-H	-832.723	1.08	-713.482	119.24
C <sub>2</sub> -H <sub>7</sub>	-832.723	1.11	-754.413	78.31
C <sub>3</sub> -Br	-832.723	1.958	-751.858	80.865
C <sub>3</sub> -H <sub>9</sub>	-832.7	1.1	-726.168	106.555
C <sub>1</sub> -C <sub>2</sub>	-832.72	1.463	-727.399	105.323
C <sub>2</sub> -C <sub>3</sub>	-821.841	1.363	-723.895	97.946

The second photodissociation path is the dissociation of C<sub>2</sub>-H<sub>7</sub> to form 3-bromopropene compound and released hydrogen radical. The geometry optimized of 3-bromopropene have been calculated with *Ab initio* method as represented in Fig.5. The third photodissociation pathway is the breakdown of C<sub>2</sub>-C<sub>3</sub> to give us

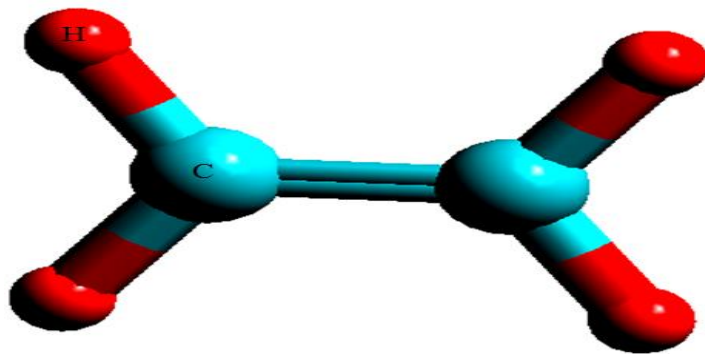
ethene and CH<sub>2</sub>Br radical. Geometry optimized of the ethene molecule has been computed by using density functional theory as given in Fig.6. The dipole moment calculation gives zero value due to symmetry in electronic density distribution among the ethene molecule.



**Figure 4 :** Potential energy surface of 3-bromopropene radical calculated at PM3/CI (4\*4) method.



**Figure 5:** Geometry optimized of 3-bromopropene calculated at *Ab initio*/3-21G(d) method.





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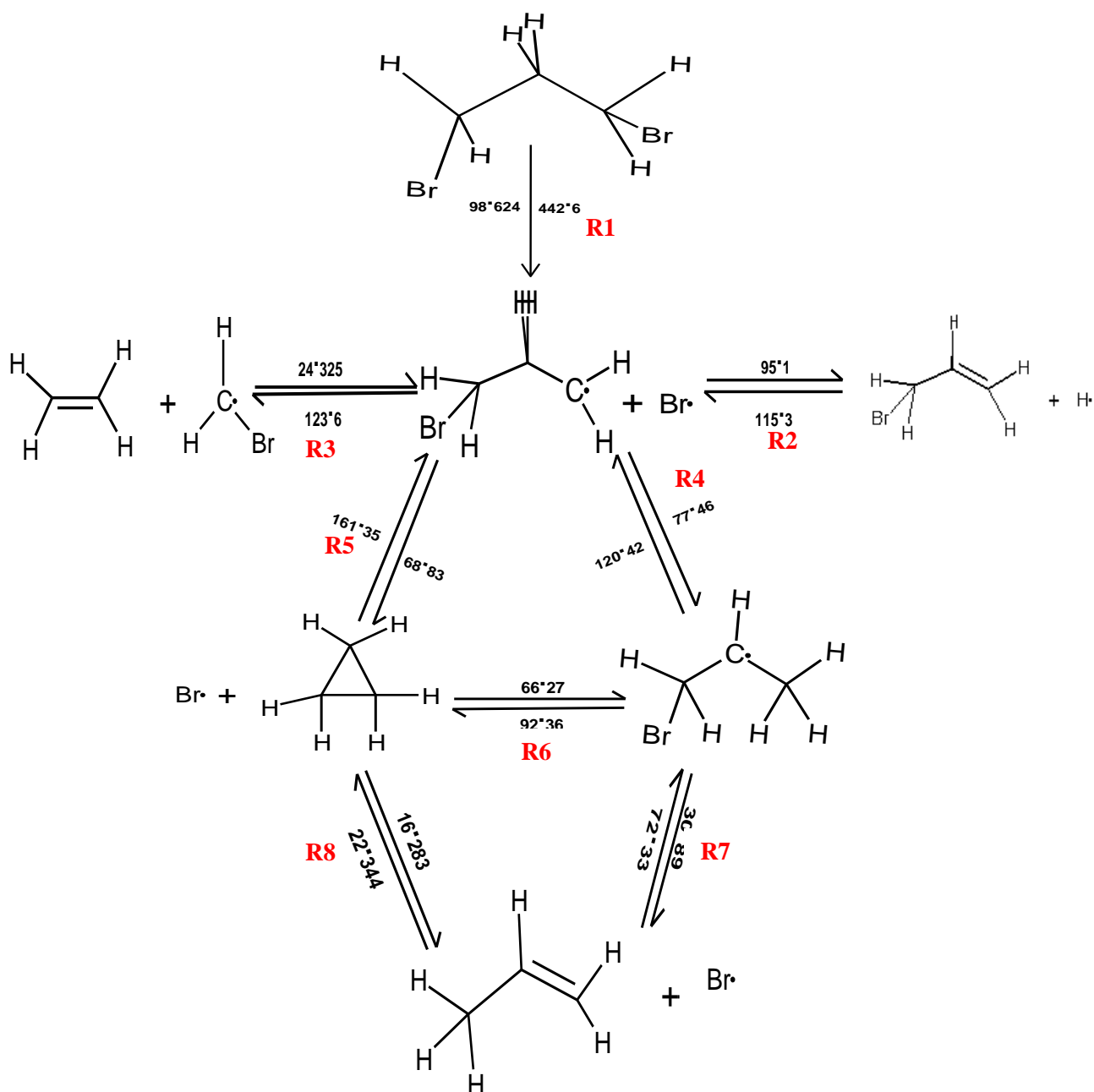
**Figure 6 : Geometry optimized of ethene predicted at DFT / B3LYP /6-31 G\* level of theory.**

The fourth photodissociation pathway is a rearrangement reaction of primary radical to give a secondary radical which is more stable. The secondary radical has two pathways, the first pathway is R6 to give cyclopropane and bromine radical. The second path of secondary free radical is a conversion into a propene molecule and released bromine radical R7 reaction. The suggested fifth pathway of photolysis is a direct transformation of primary free radical into a cyclopropane which is the preferred and the most probable pathway while the last pathway is the isomerization of cyclopropane to propene.

The isomerization of cyclopropane to propene directly has an energy barrier equal to 64-66 kCal mol<sup>-1</sup> which is calculated experimentally. The energy

barrier computed by MNDO/d method recorded lower value compared with the experimental value, to obtain an approximated value *Ab initio* or DFT computational methods must be used [24] . The suggested photolysis reactions summarized all the photolysis pathways as given in scheme 1.

The thermodynamic functions of the proposed reactions have been calculated by using a PM3 method as shown in Table 6, where the rearrangement (R4) reaction of primary radical to secondary radical is exothermic and spontaneous reaction. The reactions of cyclopropane with bromine radical (R6, R8) also, exothermic and spontaneous reaction.



**Scheme1.** The proposed photolysis mechanism with energy barrier of 1,3-DBP calculated at semiempirical MNDO/d method.

**Table 6: Thermodynamic functions of the photodissociation pathways of 1,3-DBP compound calculated at PM3/CI method at STP conditions.**

Reactions*		$\Delta H_r$	$\Delta G_r$	$\Delta S_r$
<b>R1</b>	$\text{CH}_2\text{Br}-\text{CH}_2-\text{CH}_2\text{Br} \xrightarrow{h\nu} \text{CH}_2\text{Br}-\text{CH}_2-\dot{\text{C}}\text{H}_2 + \text{Br}\cdot$	52.95	55.156	-0.0074
<b>R2</b>	$\text{CH}_2\text{Br}-\text{CH}_2-\dot{\text{C}}\text{H}_2 \longrightarrow \text{CH}_2\text{Br}-\text{CH}=\text{CH}_2 + \text{H}\cdot$	40.599	41.395	-0.0027
<b>R3</b>	$\text{CH}_2\text{Br}-\text{CH}_2-\dot{\text{C}}\text{H}_2 \longrightarrow \cdot\text{CH}_2\text{Br} + \text{CH}_2=\text{CH}_2$	34.252	23.322	0.0367
<b>R4</b>	$\text{CH}_2\text{Br}-\text{CH}_2-\dot{\text{C}}\text{H}_2 \longrightarrow \text{CH}_2\text{Br}-\dot{\text{C}}\text{H}-\text{CH}_3$	-8.612	-9.331	0.00241
<b>R5</b>	$\text{CH}_2\text{Br}-\text{CH}_2-\dot{\text{C}}\text{H}_2 \longrightarrow \text{Cyclopropane} + \text{Br}\cdot$	21.553	26.66	-0.0171
<b>R6</b>	$\text{Cyclopropane} + \text{Br}\cdot \longrightarrow \text{CH}_2\text{Br}-\dot{\text{C}}\text{H}-\text{CH}_3$	-30.17	-35.98	0.0195
<b>R7</b>	$\text{CH}_2\text{Br}-\dot{\text{C}}\text{H}-\text{CH}_3 \longrightarrow \text{H}_3\text{C}-\text{CH}=\text{CH}_2 + \text{Br}\cdot$	14.807	20.293	-0.0184
<b>R8</b>	$\text{Cyclopropane} + \text{Br}\cdot \longrightarrow \text{H}_3\text{C}-\text{CH}=\text{CH}_2 + \text{Br}\cdot$	-15.358	-15.69	0.0011

\*Thermodynamic functions in kCal mol<sup>-1</sup> units.**Conclusion:**

- 1- 1,3-dibromopropane exists in three conformations C<sub>2</sub>, C<sub>1</sub> and C<sub>2v</sub> which is found in this study that the C<sub>2</sub> conformation is more stable than other conformations which is proved with a total energy being equal to -26652.031 kCal mol<sup>-1</sup>.
- 2- 1,3-dibromopropane breakdown at a wavelength equal to 442.571 nm to released bromine and 3-bromopropane radicals with activation energy equal to 98.624 kCal mol<sup>-1</sup>.
- 3- There are eight pathways in photolysis mechanism of 1,3-DBP, three of them through C-Br bond which give us different products, the other pathway is through C-H,C-C bonds, also rearrangement, transformation and isomerization pathway.
- 4- The most probable photolysis pathway is through R5 which give us cyclopropane and then isomerization to propene due to lowest value of activation energy.

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