

## Xanthyliadeneadamantane-1, 2-dioxetane (XAD) Chemiluminescent Decomposition Mechanism– A DFT Study

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### Abstract

The Xanthyliadeneadamantane- 1, 2-dioxetane (XAD) is decomposition mechanism examined by long-range-corrected hybrid functional LC-wPBE /6-31+G\* method using Gaussian 09. The energetics of the decomposition reaction through transition states/intermediates at the lowest singlet and triplet states is studied with full optimization as well as frequency analysis. Thus, our calculations indicate that the chemiluminescent decomposition of XAD occurs via a biradical pathway.

**Keywords:** Chemiluminescent, xanthyli, XAD, biradical pathway, long-range-corrected hybrid functional.

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### Introduction

Chemiluminescent reactions (CL), which involve chemical changes leading to light emission, are closely related to peroxide chemistry, particularly cyclic four-membered peroxide chemistry. Although CL and bioluminescence have been known for a long time<sup>1,2,3</sup>, mechanistic research into generating electrically excited states through chemical or enzymatic transformations began with the creation of these four-membered ring peroxides<sup>4,5</sup>.

Significant theoretical and experimental efforts have been made over the last 25 years to better understand the mechanism of four-membered ring peroxide cleavage. Turro<sup>6</sup> first postulated a concerted mechanism, and Richardson<sup>7,8</sup> first proposed a biradical mechanism. The concerted mechanism is a one-step reaction in which the C-C and O-O bonds dissolve at the same time. The two-step biradical process, on the other hand, proposes that once the O-O link is broken before the C-C bond is broken results in the formation of a biradical intermediate. The generated intermediate is then expected to split between excited state carbonyl compounds.

Schuster et al. (Schuster, 1979)<sup>9</sup> proposed a different mechanism called chemically triggered electron exchange luminescence (CIEEL). The process starts with a one-electron transfer (ET) from a suitable donor molecule (activator, ACT) to a high-energy organic molecule (peroxide for example). Following the rearrangement or loss of a neutral fragment (e.g., carbon dioxide), the reduced peroxide is converted to a powerfully reducing species in the form of a radical anion. Following charge annihilation, an electrically excited state of ACT is created, and the chain concludes with ACT emission.

### Computational Methods

The long-range-corrected hybrid functional LC-wPBE<sup>10</sup> is more precise for representing a wide range of molecular activities, such as long-range charge transfer, thermochemistry, reaction barrier heights, and bond lengths.

The calculations were carried out using Gaussian 09 program<sup>11</sup>. LC-wPBE/6-31+G\* is the method used to optimize, the ground state and the transition states. Geometry optimizations of the stationary points along <sup>3</sup>BR (biradical), <sup>3</sup>TS1 (triplet transition state), and <sup>1</sup>TS1 (singlet transition state) were performed using ULC-wPBE/6-31+G\*. The optimized geometries were analysed by vibrational frequencies. The decomposition reaction of (S<sub>0</sub>) and triplet (T<sub>1</sub>) states was investigated, by the stretching of C-C and O-O bonds.

## Results and Discussion

### 1. Optimized geometries of XAD using LC-wPBE/6-31+G\* in the ground (S<sub>0</sub>) state:

Figure 1 display optimal geometry of the XAD ground state structures. Table 1 provides a list of the XAD's geometrical parameters.

The X-ray structural data value for XAD (1.575 Å) is 0.010 Å shorter than the C1-C2 bond's length of 1.565 Å in XAD<sup>12</sup>, whereas the C2-O3 length of the xanthyl side is 1.439 Å and is 0.0029 Å shorter than the X-ray structure (1.468 Å), the C1-O4 length of the adamantyl side is 1.456 Å and is quite similar to the observed value (1.466 Å). The experimental value is 1.507 Å which is 0.064 Å longer than the measured O3-O4 bond length of 1.443 Å in XAD. It is observed that, the dioxetane ring is twisted out of plane rather than being planar, as shown in Table 1.

The xanthyl and spiro-adamantyl substituents steric interaction is not the cause of the four-membered ring's deformation. However, it is caused by an unfavourable nonbonded interaction between pairs of equatorial adamantyl group hydrogens and xanthyl group hydrogens that are situated beneath the dioxetane ring. The ring angles of the dioxetanes C1-C2-O3 and C2-C1-O4 are 86.7° and 87.3°, respectively, and they are extremely similar to those of the mono- and tetra-substituted dioxetanes (87.5°–90.1°). The dioxetane ring has a dihedral angle of -11.2°.

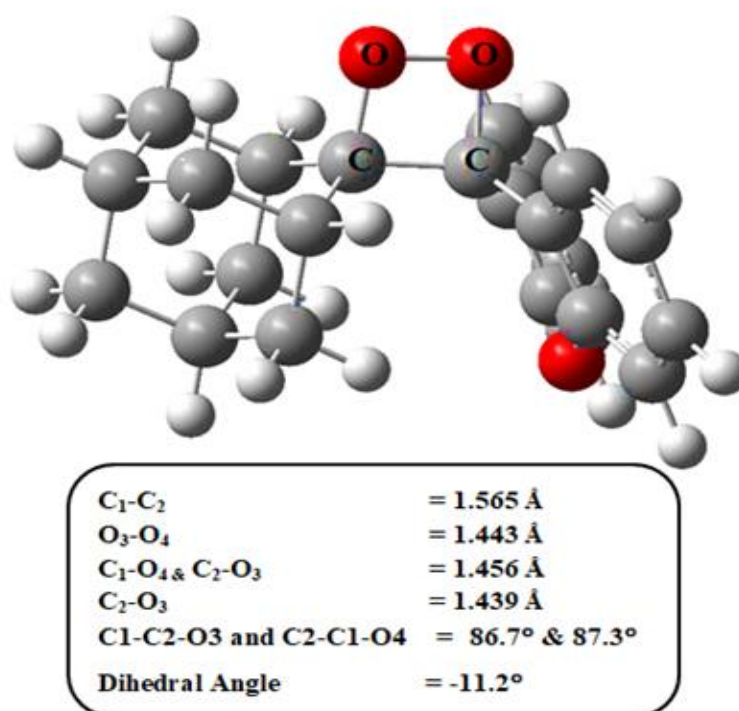


Figure 1: Optimized geometrical parameters of the XAD using LC-wPBE/ 6-31+G\*

**Table 1: Bond lengths (Å) and angles (°) in the dioxetane XAD.**

Parameters	XAD	XAD <sup>a</sup>
C1-C2	1.565	1.575
C1-O4	1.456	1.466
C2-O3	1.439	1.468
O3-O4	1.443	1.507
C1-C2-O3°	86.7	--
C2-C1-O4°	87.3	--
O3-O4/ C1-C2	0.922	--
O4-C1-C2-O3°	-11.2	14.8
Energy (Hartree)	-1114.5815795	--

**a- X-ray crystal structure of XAD<sup>12</sup>.**

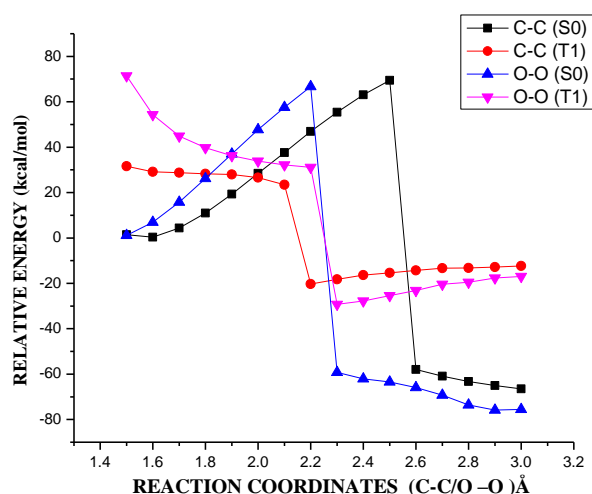
**2. XAD's Structural changes and variation in energies beside the reaction path**

Figure 2 shows the variation in the relative energies of XAD along the reaction coordinate as a function of O-O stretch and C-C stretch for ground state ( $S_0$ ) and triplet state ( $T_1$ ).

The C-C bond length increases from 1.562 Å to 2.958 Å when the O-O bond of XAD in the ground state ( $S_0$ ) is stretched from 1.5 Å to 3.0 Å. In the ground state, the C1-O4 and C2-O3 lengths change to 1.212 Å and 1.212 Å respectively, resulting in the two carbonyl fragments adamantanone (AD) and Xanthone (XA). When O-O bond length is 2.3 Å, energy drops to 59.2 kcal/mol. The C-C length is stretched out as the O-O length is stretched further, increasing the dihedral angle O4-C1-C2-O3 to 165.1°.

In the triplet state, the energy decreases as the O-O bond length rises from 1.5 Å to 3.0 Å, whereas the C1-C2 length only undergoes a little shift. The energy rises up to 2.2 Å in the case of C-C stretching coordinate along the  $S_0$  state. The energy decreases to 29.2 kcal/mol when the bond length of O-O becomes 2.3 Å, and the C-C length is extended to 2.969 Å. In the fragments of adamantanone (AD) and xanthone (XA) the C-O bond lengths of 1.215 Å and 1.216 Å, respectively. Changes are made to the dihedral angle, which goes from -12.9° to -164.1°.

Yet, the triplet state's energy along the C1-C2 stretching path rises by up to 2.1 Å. The energy falls as the stretch is increased to 2.2 Å, and the C1-O4 and C2-O3 bond lengths are 1.243 Å and 1.261 Å respectively.



**Figure 2** Variation of the relative energies for the decomposition of XAD

### 3. XAD's intermediates and transition states along the chemical path

Using the LC-wPBE/6-31+G\* and ULC-wPBE/6-31+G\* techniques, the transition states along the reaction pathways for the chemiluminescent decomposition of XAD were examined. By optimizing the structure along the reaction path, the transition states  $^1\text{TS1}$ ,  $^1\text{TS3}$ ,  $^1\text{TS2}$ ,  $^3\text{TS1}$  and a triplet biradical intermediate ( $^3\text{BR}$ ) were identified. ULC-wPBE/6-31+G\* computation is used to characterise them. Table 2 includes a list of the geometrical characteristics of the transition states of  $^1\text{TS1}$ ,  $^3\text{TS1}$ ,  $^1\text{TS3}$  and a triplet biradical intermediate ( $^3\text{BR}$ ), which are also shown in Figure 3. Figure 4 depicts the Potential Energy Diagram for the decomposition of XAD.

By stretching the O-O bond,  $^1\text{TS1}$  is created from the reactant's ground state. In  $^1\text{TS1}$ , the C-C separation is 1.617 Å. The lengths of C1-O4 and C2-O3 are 1.373 Å and 1.416 Å, respectively. C1-C2-O3 and C2-C1-O4 have dioxetane ring angles of  $99^\circ$  and  $103^\circ$ , respectively. The dihedral angle O4-C1-C2-O3 ( $0.3^\circ$ ) and the O-O bond length is 2.098 Å define the geometry of  $^1\text{TS1}$ . 30.5 kcal/mol is the potential barrier value. The aforementioned activation barrier is 7.5 kcal/mol higher than the 23 kcal/mol experimental activation energy for XAD<sup>129</sup>.

Intersystem crossover produces a biradical minimum ( $^3\text{BR}$ ) from the  $^1\text{TS1}$ . The bond lengths C1-C2, O3-O4, C1-O4, and C2-O3 are 1.614 Å, 2.402 Å, 1.373 Å, and 1.416 Å in the triplet biradical ( $^3\text{BR}$ ). From the angles of  $99.0^\circ$  and  $103.0^\circ$  of  $^1\text{TS1}$ , the dioxetane ring angles C1-C2-O3 and C2-C1-O4 of XAD are increased to  $103.5^\circ$  and  $102.1^\circ$ , respectively. 25.5 kcal/mol is the potential barrier.

Stretching the C-C length from the  $^3\text{BR}$  led to the triplet transition state ( $^3\text{TS1}$ ). The C1-C2 and O3-O4 bond lengths of  $^3\text{TS1}$  are 2.496 Å and 2.098 Å respectively. The bond lengths of C1-O4 and C2-O3 are 1.232 Å and 1.286 Å. The adamantanone (AD) is in the triplet ( $T_1$ ) state, according to the aforementioned C-O lengths, whereas the Xanthone is in the singlet ground ( $S_0$ ) state. The energy difference between  $^3\text{TS1}$  and  $^3\text{BR}$  is 1.8 kcal/mol. One imaginary vibrational frequency  $187.3 \text{ i cm}^{-1}$  along the C-C stretching coordinate confirm the transition state,  $^3\text{TS1}$ . It is reported that the energy of the  $^3\text{BR}$  intermediate of the dioxetanes having the adamantyl group is 20 to 25 kcal/mol higher than that of the simple dioxetanes.

In open-shell singlet state ( $^1\text{TS3}$ ), the lengths of C1-C2, O3-O4, C1-O4, C2-O3, and C2-O3 are 1.694 Å, 2.083 Å, 1.386 Å, and 1.395 Å respectively. The C1-C2-O3 and C2-C1-O4 dioxetane ring angles of XAD are  $96.3^\circ$  and  $94.1^\circ$  respectively. The experimental value (23.8 kcal/mol) and the predicted energy barrier for the production of  $^1\text{TS3}$  from  $S_0$  are both 25.2 kcal/mol<sup>129</sup>. Due to stretching of both C-C and O-O lengths, one imaginary frequency  $409.5 \text{ i cm}^{-1}$  is obtained.

In this study, the thermal decomposition of XAD was also described. Both Table 2 and Figure 3 show the geometrical characteristics of the closed-shell transition state  $^1\text{TS2}$  that are involved in the

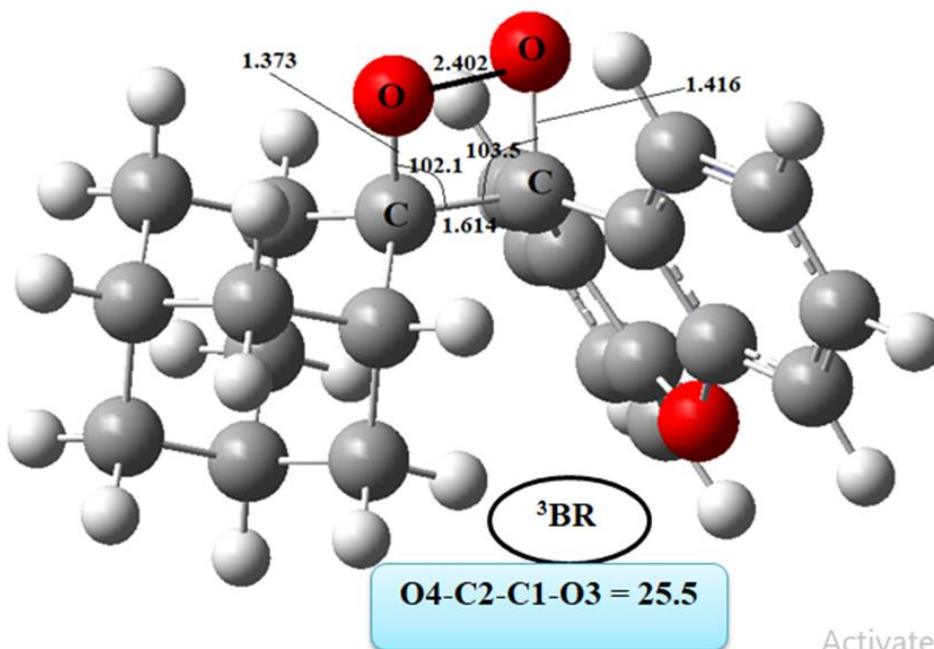
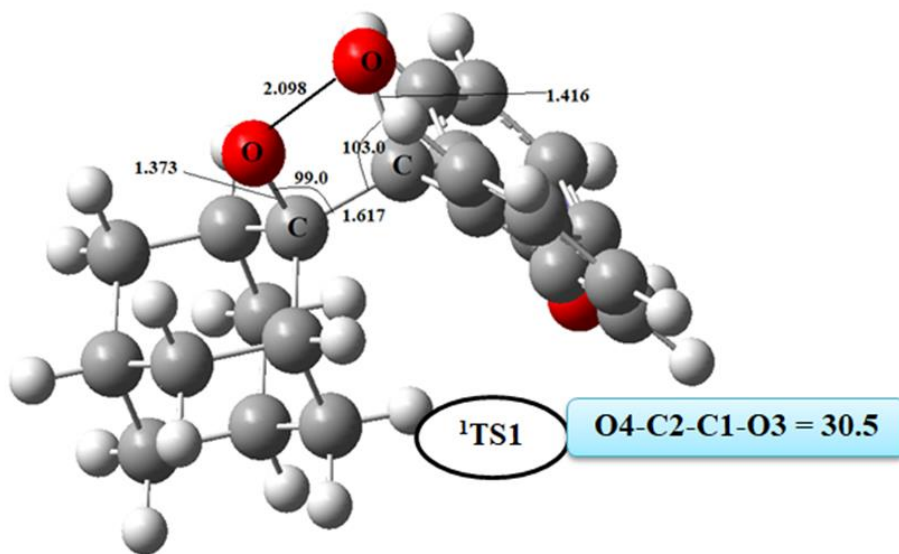
thermal decomposition. The O3-O4 and C1-C2 lengths are respectively 1.920 Å and 1.913 Å. For <sup>1</sup>TS2, the potential barrier is 38.0 kcal/mol. Due to lengthening the lengths of both the C-C and O-O, one imaginary frequency (1346.2 i cm<sup>-1</sup>) is obtained. According to the vibrational study, XAD has a concerted pathway for thermal decomposition.

**Table 2** Energies, selected bond lengths (Å) and angles (°) of different transition states and triplet biradical of XAD using ULC-wPBE/6-31+G\*. Bond length in Å, bond angle and dihedral angle in degrees, total energy in Hartree, and relative energy (RE) in kcal/mol.

TS/BR	<sup>1</sup> TS1	<sup>1</sup> TS3	<sup>3</sup> TS1	<sup>3</sup> BR	<sup>1</sup> TS2
C1-C2	1.617	1.694	2.096	1.614	1.913
C1-O4	1.373	1.386	1.232	1.373	1.334
C2-O3	1.416	1.395	1.286	1.416	1.385
O3-O4	2.098	2.083	2.496	2.402	1.920
C1-C2-O3°	103.0	96.3	93.5	103.5	95.1
C2-C1-O4°	99.0	94.1	89.3	102.1	93.4
O4-C1-C2-O3°	0.3	-30.0	-62.3	38.9	-28.5
ZPE	0.3976749	0.397673	0.395958	0.050104	0.40532
Frequency	376 i	409.5 i	187.3 i	34.2 i	1346.2 i
RE	30.5	25.2	24.3	25.5	38

a. For closed-shell singlet transition state, <sup>1</sup>TS2, LC-wPBE/6-31+G\* method is used.

b. Reference energy is -1114.5815795 a.u. for S<sub>0</sub> ground state using LC-wPBE/6-31+G\* method.



Activate V



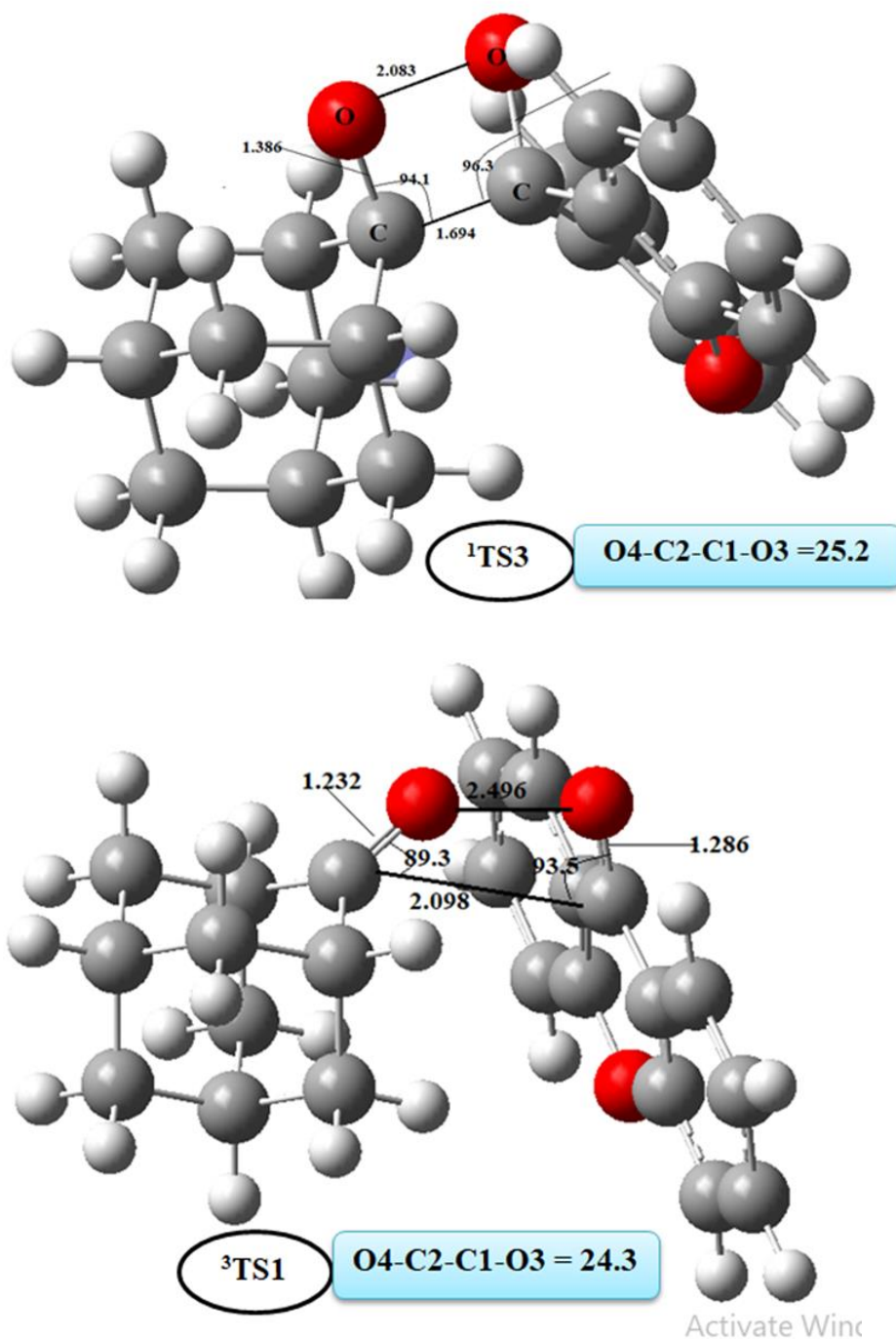


Figure 3 Optimized geometrical parameters of the dioxetane ring in the <sup>1</sup>TS1, <sup>3</sup>BR, <sup>1</sup>TS3 and <sup>3</sup>TS1 of XAD. Bond length in Å, bond angle and dihedral angle in degrees.

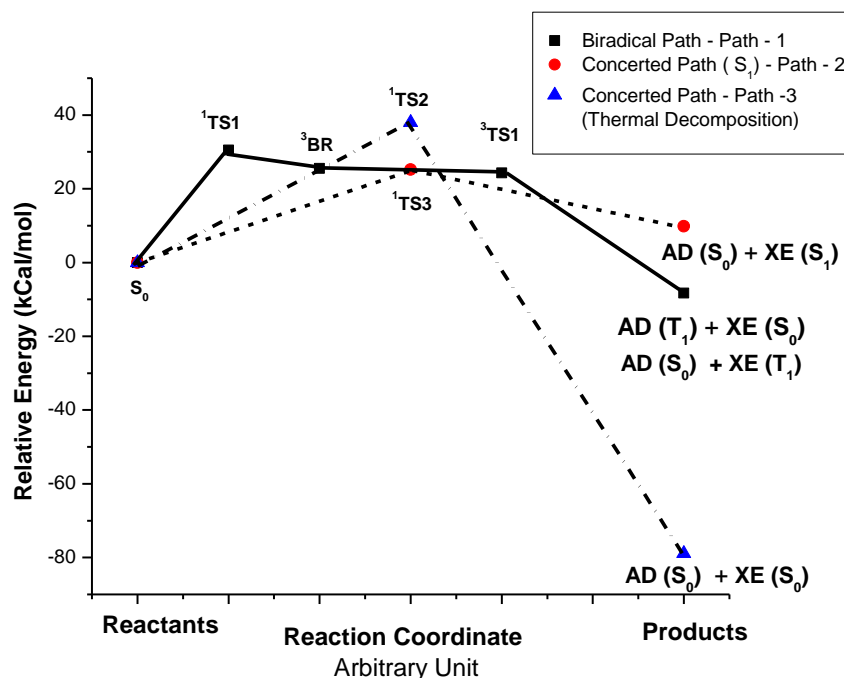


Figure 4 Potential Energy Diagram for the decomposition of XAD

4. Products formed from the dissociation of XAD:

Table 3 provides a summary of the calculations performed on the total energy of the products generated during the thermal and chemiluminescent decomposition of the dioxetane XAD. Figure 5 depicts the geometrical structures of adamantanone (AD) and Xanthone (XA).

The C1-O4 length of adamantanone (AD) in the  $S_0$  state is 1.218 Å. For the  $S_1$  and  $T_1$  states of 2-Adamantanone, the value has been increased to 1.299 Å and 1.301 Å respectively. From 1.528 Å in the  $S_0$  of AD, the C atoms bonded with C1 atom of dioxetane ring have marginally increased to 1.548 Å and 1.564 Å in the  $S_1$  and  $T_1$  states, respectively. 2-Adamantanone has triplet excitation energy of 3.16 eV, which is 0.14 eV less than the experimental value of 3.30 eV<sup>13</sup>.

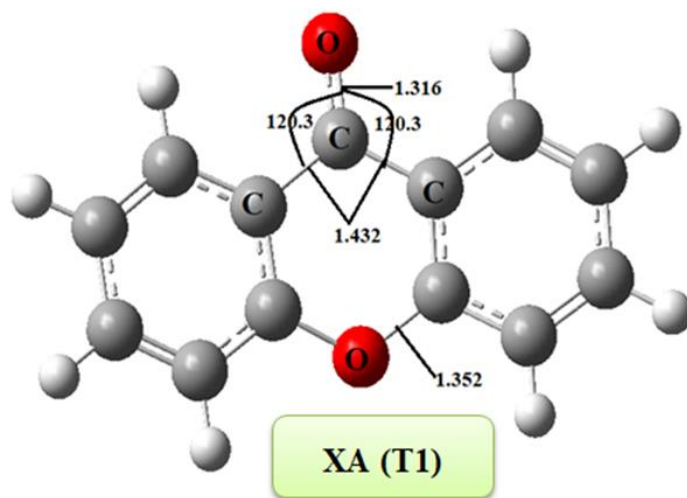
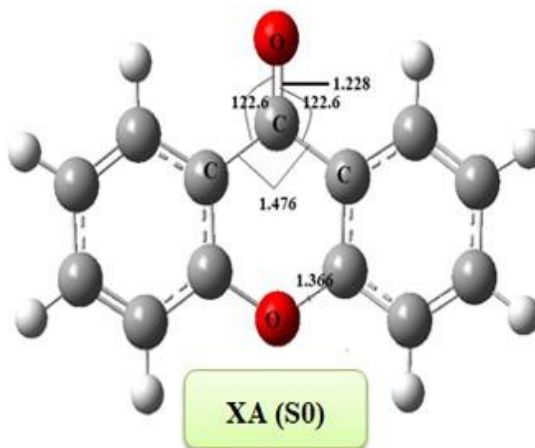
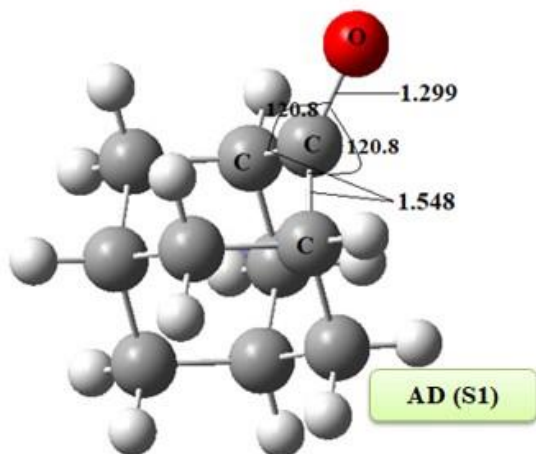
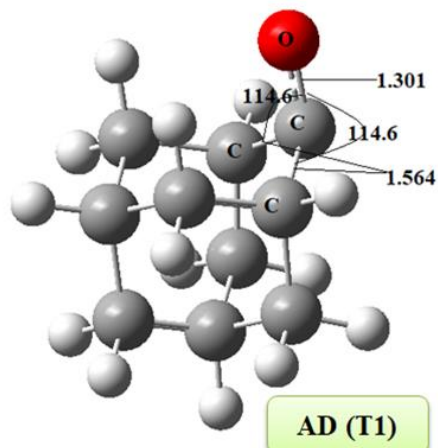
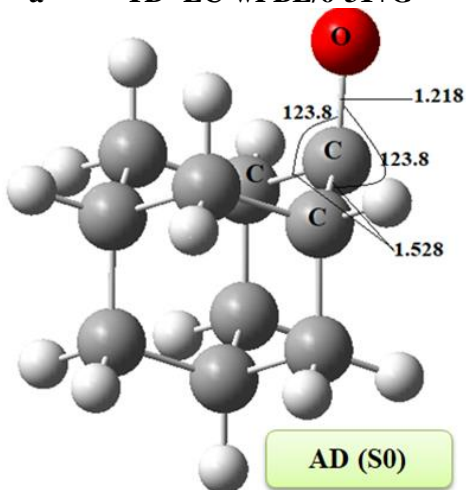
The singlet excitation energy of AD is 3.59 eV which is 0.25 eV lesser than the experimental value (3.84 eV)<sup>13</sup>. The triplet excitation energy of Xanthone is 3.38 eV, 0.16 eV larger than the experimental value (3.22 eV)<sup>12</sup>. Whereas the excitation energy in  $S_1$  state is 3.36 eV, 0.32 eV less than the experimental result (3.040 eV)<sup>13</sup>.

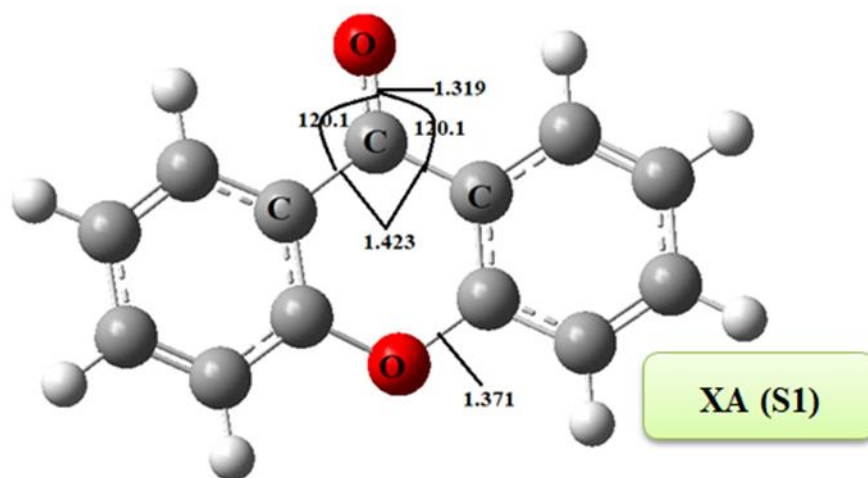
Table 3 Total Energies of 2-Adamantanone (AD), Xanthone (XA); LC-wPBE/6-31+G\* for  $S_0$  and ULC-wPBE/6-31+G\* for  $T_1$  states.

Products	Energy (Hartree)	Relative Energy (kcal/mol)
AD ( $S_0$ ) + XA ( $S_0$ )	-1114.7073145	-78.9
AD* ( $T_1$ ) + XA ( $S_0$ )	-1114.5683526	-8.3
AD ( $S_0$ ) + XA* ( $T_1$ )	-1114.5658028	-9.9
AD* ( $T_1$ ) + XA* ( $T_1$ )	-1114.4808639	63.2
AD* ( $S_1$ ) <sup>a</sup> + XA ( $S_0$ )	-1114.5659622	9.8
AD ( $S_0$ ) + XA ( $S_1$ )	-1114.5790297	-1.6
AD* ( $S_1$ ) + XA* ( $S_1$ )	-1114.4411833	88.1



a- TD- LC-wPBE/6-31+G\*



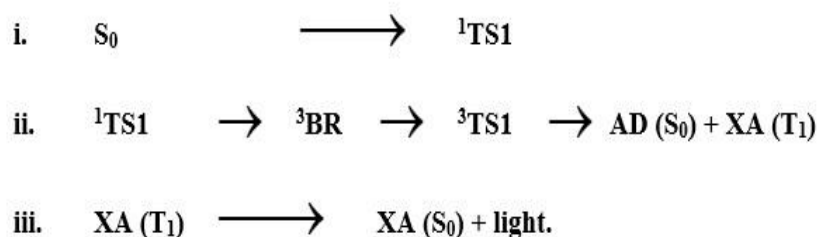


**Figure 5 Geometrical structures of the products AD and XA in  $S_0$ ,  $T_1$  and  $S_1$  states.**

### 5. Mechanism

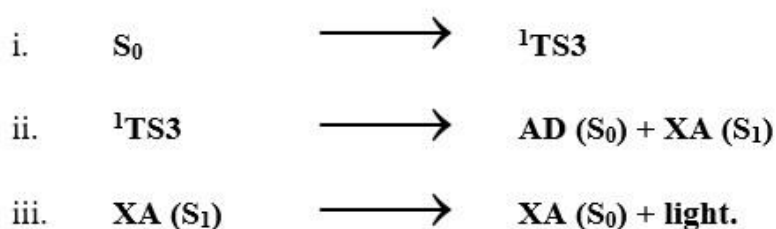
Two pathways for the chemiluminescent decomposition of XAD can be inferred from the foregoing. The first mechanism, which involves a triplet biradical intermediate  $^3BR$ . The O-O stretch from the reactant minimum controls the initial portion of the reaction coordinate, resulting in the transition state  $^1TS1$ .

By cleaving the O-O bond from the  $^1TS1$ , the biradical triplet ( $^3BR$ ) is created. The C-C bond in the intermediate  $^3BR$  is stretched, resulting in  $^3TS1$ , which produces two products, one in the triplet ( $T_1$ ) state and the other in the ground ( $S_0$ ) state. 2-adamantanone ( $S_0$ ) and xanthone ( $T_1$ ) state are the results of the chemiluminescent decomposition of XAD. The experimental findings, which show that 2-adamantanone emits fluorescence when it is in the  $S_1$  state, are in contrast to the results reported for the chemiluminescent decomposition of XAD. In Scheme 1, the chemiluminescent characteristic of XAD is explained.



### Scheme 1

The second mechanism, which follows a concerted pathway, is comparable to that of AAD. In the first phase, a concerted stretching of the C-C and O-O bond lengths results in the transition state  $^1TS3$ . The products of this transition state are Xanthone in the ground ( $S_0$ ) state and adamantanone in the singlet excited state ( $S_1$ ) state. The experimental results<sup>30</sup> make it clear that the chemiluminescent decomposition of XAD results in the production of xanthone in the singlet excited state ( $S_1$ ) and adamantanone in the singlet ground state ( $S_0$ ). Scheme 4.2 depicts the mechanism underlying the chemiluminescent property of XAD.



Scheme 2

### Conclusions

It is noticed that the mechanism of the chemiluminescent decomposition of XAD follows biradical pathway based on **Scheme 1**. A triplet biradical-intermediate serves as the reaction's intermediary. Only the dissociation of the triplet transition state,  ${}^3TS1$ , produces the products. The available experimental activation energy of 24.3 kcal/mol. The above mechanism proposal is justified by the fact that the reaction adopts a lower energy pathway to generate the products

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