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Density Functional Theory Investigation on the Mechanism of Chemiluminescent Decomposition in Adamantylideneadamantane-1,2-Dioxetance (BAAD) and Monoadamantylidene-1,2-Dioxetane (MAD)

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ABSTRACT

Chemiluminescence is the emission of light as a result of chemical reaction. The 4-membered dioxetane ring is also proposed as an intermediate in the chemiluminescent reactions. Bisadamantylidene Adamantane 1,2-Dioxetane (BAAD) have received special attention. The former is a very stable compound having half-life time of approximately 104 years at room temperature. The main aim of this study was to investigate the mechanism of chemiluminescent decomposition of dioxetane derivatives BAAD. The ground and the transition states in the closed shell singlet state were optimized by B3LYP/6-31G method.

Key words: Chemiluminescence, dioxetane, Bisadamantylidene adamantane 1,2-dioxetane, closed shell singlet state.

INTRODUCTION

Chemiluminescence is the emission of light as a result of chemical reaction [1]. There is no external light source used to initiate a chemiluminescence reaction. These reactions are generated by fundamental molecular transformations. In these reactions, “non-adiabatic surface jump” leads to the ground state reactant into excited state. Traditionally developed methods for atmospheric ozone and nitric oxide provide a good example of the advantage of CL reactions [2]. The 4-membered dioxetane ring is also proposed as an intermediate in the chemiluminescent reactions [3-10]. More results have been published on the experimental and theoretical studies of chemiluminescence of 1, 2-dioxetanes [11-15].

Thefirstdioxetanenamely 3, 3, 4-trimethyl 1,2-dioxetaneby Kopeckyand Mumford [16] in 1969, whichdecomposes rapidly at room temperature. In 1973, Turro and Lechtken [17-18] studied the decomposition and chemiluminescence of TMD was strongly solvent dependent, activation energy of TMD 25 kcal/mol has been measured and a reaction enthalpy of 60 kcal/mol was calculated [19]. In the case of simple dioxetanes chemiluminescence emission is from triplet state *via* biradical mechanism [20] Most studies showed that 3,3,4-trimethyl 1,2-dioxetane, TMD and simple dioxetane derivatives yield triplet products upon decomposition in solution [21-23]. More succeeding researches reveal that, thermal decomposition studies [24] on TMD using MCSCF method is used to study the mechanism of singlet state (S_1) formation.

According to the theoretical point of view 1,2-dioxetane (DO) and TMD are studied by using stepwise mechanism [24].

According to Tanaka and Tanaka [24] report, TMD is more stable than DO and the chemiluminescence yield is much higher when compared with DO. This report also proves that TMD follows biradical mechanism and it form the biradical was formed by the breaking of O-O bond in the rate determining step of the chemiluminescent reaction. TMD is more stable than parent system, because in contain more number of methyl substitution. More experimental results [25] are also reported on TMD that, the triplet yield for TMD is significantly higher than that for the parent system.

In the case of adamantyl substituted dioxetanes, such as spiro-adamantyl, spiro-acridyl and spiro-xanthyl are used as thermochemiluminescent immunoassays [26]. Bisadamantylidene Adamantane 1,2-Dioxetane (BAAD) was studied by Wynberg and coworkers [27-32] by using X-ray crystallography. In 1983, Adam [33] resolves the stability of BAAD. He proposed that, the biradical is formed after the breakage of O-O bond leads to fragmentation at transiod conformation rather cisoid conformation. The unusual thermal stability [32] of BAAD is due to the compression of bulky spiroadamantane units. X-ray structure [34] reveals that, BAAD is not planar and this compound also follows biradical mechanism, the initial O-O bond cleavage results a dioxyl biradical leads to energetically unfavorable compression they increase the activation energy. The length of O-O bond is 1.48 Å, average length of C-C bonds in the adamantyl group is 1.531 Å and the central C-C bond length is 1.549 Å. In BAAD [35], the ring opening mechanism invokes compression of the alkyl substituents in the initial step was the breaking of O-O bond either in concert with the spin flip (or) to form a singlet biradical. But the O-O and C-C bonds cleaves simultaneously it leads to steric compression. In 1982, Adam et al tried to synthesize the Monoadamantyl 1,2-Dioxetane (MAD) *via* Kopecky route still a failure process [36].

According to the theoretical point of view [24,37-43] and most previous studies showed that there are three mechanisms involved in the decomposition of 1,2-dioxetanes. In stepwise mechanism, according to White and Harding [44] and Richardson and O'Neal [20], cleavage of the weak O-O bond generates a short lived biradical intermediate which cleaves rapidly to carbonyl containing products. The initially formed singlet biradical is postulated to partition between singlet ground state and excited state carbonyl products. Singlet and triplet of the biradical should approach each other in energy with sufficient spatial separation of the oxygen atom. Hence, intersystem crossing to the triplet *via* spin-orbit coupling will be facilitated in the biradical. Cleavage of the triplet biradical should lead to the formation of a triplet excited state products. The asynchronous concerted mechanism was proposed by Adam [25]. It stated that, the first part of the chemiluminescent reaction should be concerted; the O-O bond will extend while the C-C bond undergoes some stretching. This is followed by a biradical phase (where the O-O bond is broken) prior to the decomposition (C-C bond breaking) into excited state products. The CIEEL mechanism, proposed by Schuster et al. , the sequence of reaction was initiated by one-electron transfer from a suitable donor molecule (activator ACT) to an organic molecule of high energy content. Subsequent rearrangement (or) loss of a neutral fragment transforms the reduced peroxide into a highly reducing species; in the form of a radical anion charge annihilation then generates an electronically excited state of ACT and the final step of the sequence is the emission from the ACT.

Among the derivatives, Bisadamantylidene Adamantane 1, 2-Dioxetane (BAAD) have received special attention. The former is a very stable compound having half-life time of approximately 10^4 years at room temperature. When it is heated to about 230°C, it decomposes rapidly and leads to the formation of excited state adamantanone which gives rise to chemiluminescence. The main aim of this study was to investigate the mechanism of chemiluminescent decomposition of dioxetane derivatives BAAD.

MATERIALS AND METHODS

All calculations were performed with the Gaussian 03 program [37] and Gaussian 09 program [38]. The main part of the calculations includes the geometry optimizations; vibrational frequencies and intrinsic reaction coordinate by stretching the C-C and O-O bond for the structures on the reaction path. The optimized geometries were characterized with the use of their vibrational frequencies. The ground and the transition states in the closed shell singlet state were optimized by B3LYP/6-31G* method. The open-shell systems, namely the biradical intermediate ^{3}BR, triplet transition state ^{3}TS1 and singlet biradical transition state ^{1}TS1 were optimized using UB3LYP/6-31G* calculations. The decomposition reaction of these simple dioxetanes was investigating the reaction paths by stretching the C-C and O-O bonds in the closed-shell singlet (S_0) and in the triplet (T_1) states. The ground state structures of BAAD were optimized by B3LYP/6-31+G* method.

RESULTS AND DISCUSSION

The optimized geometries of the ground state structure of BAAD are shown in Figure 1. The geometrical parameters of the dioxetane ring of these dioxetanes are listed in Table 1. The central C1-C2 bond in AAD has a length of 1.574 Ǻ which is 0.025 Ǻ greater than the X-ray structural data value of AAD (1.549 Ǻ). Boththe C1-O4 and C2-O3 lengths are having the same value of 1.472 Ǻ. The length of the O3-O4 bond of AAD is 1.481 Å, which is 0.01 Å lesser than the reported X-ray value (1.491 Å), but is equal to that in H_2O_2. The calculations reveal that the dioxetane ring is not planar, but twisted out of plane by 20.5°. This deformation is due to the unfavorable non-bonded interaction of two pairs of equatorial hydrogen of the four methylene groups located under the dioxetane ring. Thus, the puckered peroxidic ring of AAD is correctly predicted by B3LYP/6-31G* method. Both the dioxetane ring angles C1-C2-O3 and C2-C1-O4 are 86.3° which is lesser than the ring angles of mono-substituted and tetra substituted dioxetanes (87.5°- 90.1°). In TMD, only four methyl groups are present. Due to two adamantyl groups, AAD becomes more strained. The ring angles are 1.2° lesser than the angles of TMD (87.5°). Hence the agreement between the calculated and the experimental values is satisfactory.

In MAD, the C1-C2 is 1.529 Ǻ which is 0.02 Ǻ lesser than X-ray structural data value of BAAD (1.549 Ǻ). But it is very close to the theoretical value of MMD (1.524 Ǻ). The C1-O4 bond length of MAD (1.473 Ǻ) is same as the value observed in BAAD. The puckered nature is not observed in MAD and the ring is nearly planar (-0.34°). The dioxetane ring angles C1-C2-O3 and C2-C1-O4 are 90.17° and 88.23° respectively. The ground state structures of BAAD are optimized by B3LYP/6-31+G* method. The values are shown in Table 1. It reveals that the optimized geometrical parameters of BAAD is not much deviated from the results using 6-31G* basis set.

TRANSITION STATES AND INTERMEDIATE OF BAAD ALONG THE REACTION PATH

BAAD were investigated using B3LYP/6-31G* and UB3LYP/6-31G* methods. The transition states ^{1}TS1, ^{1}TS3 and 3TS1 and a triplet Biradical Intermediate (^{3}BR) were characterized along the reaction path by structural optimization using UB3LYP/6-31G* method. The transition state ^{1}TS2 was characterized by structural optimization by B3LYP/6-31G*.

^{1}TS1 is formed from the ground state of the reactant by elongation of O-O bond. The C-C distance in ^{1}TS1 is 1.593 Å. Both the C-O lengths are having the same value (1.407 Å). The dioxetane ring angles, C1-C2-O3 and C2-C1-O4 are 97.2° and 97.1° respectively. The geometry of ^{1}TS1 is characterized by the dihedral angle O4-C1-C2-O3=41.6° and the O-O distance is 2.182 Å. The potential barrier for the formation of ^{1}TS1 is 28.2 kcal/mol. It is 5.8 kcal/mol lesser than the available experimental activation energy of BAAD (34 kcal/mol).

The Biradical Minimum (^{3}BR) possesses a Relative Energy (RE) of 28.9 kcal/mol. The C1-C2, O3-O4, C1-O4 and C2-O3 lengths of ^{3}BR are, respectively, 1.615 Å, 2.338 Å, 1.375 Å and 1.375 Å. The dioxetane ring angles, C1-C2-O3 and C2-C1-O4 of ^{3}BR are increased from the value of 97.2° in ^{1}TS1 to 100.3°. From the ^{3}BR, stretching of C-C length resulted in triplet Transition State (^{3}TS1). The potential barrier for the formation of ^{3}TS1 is 28.9 kcal/mol which is 0.9 kcal/mol higher than that of ^{1}TS1. The difference between the energies of ^{3}TS1 state and ^{3}BR intermediate is only 0.7 kcal/mol. The geometrical parameters of transition states of ^{1}TS2 and ^{1}TS3 are listed in Table 2 and also depicted in Figure 2.

The potential barrier of ^{1}TS2 is 50.0 kcal/mol. A transition state, ^{1}TS3 in the singlet excited state (S_1) is optimized using the time dependent (TD)-B3LYP calculations using 6-31G* basis set. The C1-C2, O3-O4, C1-O4 and C2-O3 lengths are 2.025 Å, 2.148 Å, 1.320 Å and 1.318 Å respectively. The dioxetane ring angles, C1-C2-O3 and C2-C1-O4 of BAAD are 86.2° and 86.1° respectively. The potential barrier for the formation of ^{1}TS3 from S_0 is 38.0 kcal/mol. when single point calculation done with UB3LYP/6-31G* method is also done at the TD-B3LYP/6-31G* the barrier is lowered to 24.8 kcal/mol.

The barrier for the formation of ^{1}TS3 (24.8 kcal/mol) is lower than the barriers of ^{1}TS1, ^{3}TS1 and ^{1}TS2. The present study show that the feasibility of the chemifluorescent decomposition of AAD *via* the excited singlet transition state, ^{1}TS3. The present analysis reveals that the formation of chemifluorescence than chemiphosphorescence from BAAD has a lower activation barrier of 24.8 kcal/mol as compared to the latter having the barrier of 29.1 kcal/mol.

PRODUCTS FORMED FROM THE DECOMPOSITION OF BAAD

The total energies of the products formed from the chemiluminescence and thermal decomposition of dioxetanes, BAAD is summarized in Table 4. The geometrical structures of the 2-Adamantanone (AD) is shown in Figure 3. In the S_0 state of 2-adamantanone, the C1-O4 length is 1.216 Å. The value is increased to 1.298 Å and 1.301 Å respectively for S1 and T1 states of 2-Adamantanone. The C atoms connected to C1 atoms are slightly increased to 1.546 Å and 1.562 Å respectively for S_1 and T_1 states of AD from 1.527 Å in S_0 of AD. The triplet excitation energy of 2-Adamantanone is 3.14 eV which is 0.16 eV which is 0.28 eV lesser than the experimental value (3.84 eV).

MECHANISTIC ASPECTS OF BAAD

It is concluded that the chemifluorescence decomposition of BAAD follows a concerted mechanism proceeds via a singlet excited transition state ^{1}TS3 leading to the formation of adamantanone in the singlet excited state.

In the first step, both the C-C and O-O bond lengths are stretching in a concerted manner leading to the transition state ^{1}TS3. This transition state leads to the products, one adamantanone in the singlet excited state (S_1) state and the other adamantanone in the ground (S_0) state. The mechanism for the chemifluorescent decomposition of BAAD is shown in Scheme 1. It is evident from the experimental results that the chemiluminescent decomposition of BAAD also yields adamantanone in the singlet excited state (S_1) along with the adamantanone in the triplet (T_1) state. Chemiphosphorescence in BAAD is explained by the step-wise mechanism. From the reactant BAAD the triplet biradical 3BR is formed via the transition state ^{3}TS1 from ^{3}BR leads to the products ^{3}AD (T_1) and AD (S_0). The activation barrier for the above process is 29.1 kcal/mol which is higher than that for the formation of the products ^{1}AD (S_1) and AD (S_0).

i. $S_0 \xrightarrow{E_a = 24.8 kcal/mol} {}^1TS3$

ii. $^1TS3 \longrightarrow AD(S_1) + AD(S_0)$

iii. $AD(S_1) \longrightarrow AD(S_0)$ + light.

Scheme 1

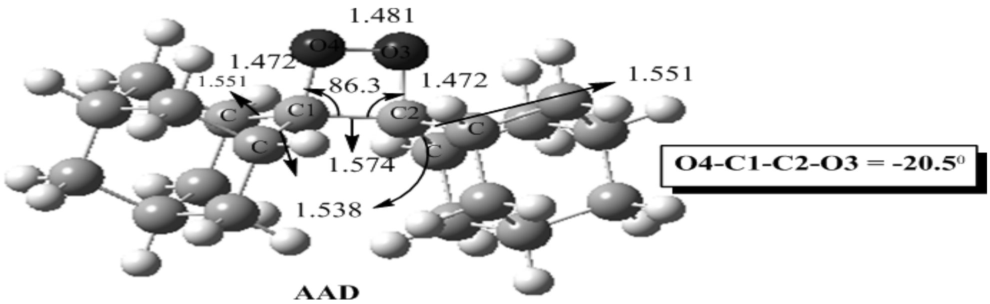
The present study predicts the preference for the chemifluorescence process than the chemiphosphorescence process in AAD. The formation of ^{1}TS1 from S_0 is the rate determining step. The activation barrier is 28.8 kcal/mol which is 5.8 kcal/mol lower than the experimental results (34 kcal/mol). The mechanism for the chemiphosphorescent decomposition of BAAD is shown in Scheme 2.

i. $\xrightarrow{E_a = 28.2 kcal/mol}$

ii. $^1TS1 \longrightarrow {}^3BR \xrightarrow{E_a = 0.2 kcal/mol} {}^3TS1 \longrightarrow AD(T_1) + FL(S_0)$

iii. $AD(T_1) \longrightarrow AD(S_0)$ + light.

Scheme 2



AAD

Figure 1. B3LYP/6-31G* optimized geometrical parameters of the BAAD. Bond length in Å, bond angle and dihedral angle in degrees.

Table 1 Selected bond lengths (Å) and angles (°) in the dioxetane BAAD

Parameters	**B3LYP/ 6-31G* optimized Geometries**	**X-ray analysis**	
	BAAD^c	**BAAD^a**	**DMTOH^b**
C1-C2	1.574 (1.578)	1.549	1.584

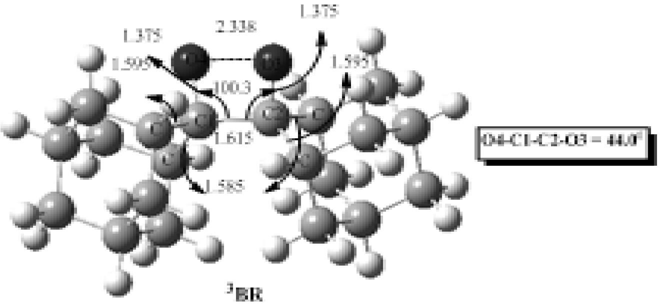
C1-O4	1.472 (1.475)	1.476	1.485
C2-O3	1.472 (1.475)	1.474	1.459
O3-O4	1.481 (1.480)	1.491	1.497
C1-C2-O3°	86.3 (86.3)	--	--
C2-C1-O4°	86.3 (86.3)		
O3-O4/ C1-C2	0.941 (0.938)	0.963	0.945
O4-C1-C2-O3°	20.5 (20.3)	21.3	7.7
Energy (Hartree)	-929.3598661 (-929.3789027)		

a: X-ray crystal structure of BAAD – adamatylideneadamantane 1,2-dioxetane
b: X-ray crystal structure of DMTOH-1-aryl-5-(9-methylfluorene-9-yl)-4,4-dimethyl-2,6,7- trioxabicyclo [3,2,0] heptanes
c: Numbers in parenthesis indicate the values in B3LYP/6-31+G(d)

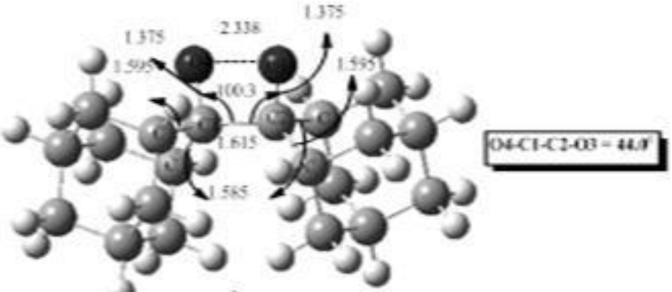
Table 2: Energies, selected bond lengths (Å) and angles (°) of different transition states and triplet biradical intermediate of BAAD using UB3LYP/ 6-31G(d)[a]. Bond length in Å, bond angle and dihedral angle in degrees, total energy in Hartree, and relative energy, relative energy[b] (RE) in kcal/moltr.

TS/BR	**^{1}TS1**	**^{1}TS3**	**^{3}TS1**	**^{3}BR**	**^{1}TS3**	**^{1}TS2**
C1-C2	1.593	1.751	1.979	1.615	2.025	1.840
C1-O4	1.407	1.347	1.337	1.375	1.320	1.345
C2-O3	1.407	1.347	1.285	1.375	1.318	1.344
O3-O4	2.182	2.115	2.148	2.338	2.148	2.011
C1-C2-O3°	97.2	92.9	88.7	100.3	86.2	86.7
C2-C1-O4°	97.1	92.9	89.4	100.3	86.1	90.8
O4-C1-C2-O3°	41.6	41.5	41.6	44.0	49.2	40.4
ZPE	0.450859	0.450865	0.451335	0.450920	0.449264	0.4482337
Frequency	401.9i	663.3i	115. 2i	67.1	919.6 i	1670.5 i
Spin densities on O_3, O_4	0.79, -0.79	0.11, -0.11	0.68, 0.72	0.85, 0.85	0.36, -0.36	--
RE (kcal/mol)	28.2	37.4	29.1	28.9	24.8[c]	50.0

a: For closed-shell singlet transition state, 1TS2, B3LYP/6-31G* method is used
b: Reference energy is -929.3598662 a.u. for S0 ground state using B3LYP/6-31G* method
c: Relative energy is calculated using TD-B3LYP/6-31G*//UB3LYP/6-31G* method



^{3}BR



^{3}BR

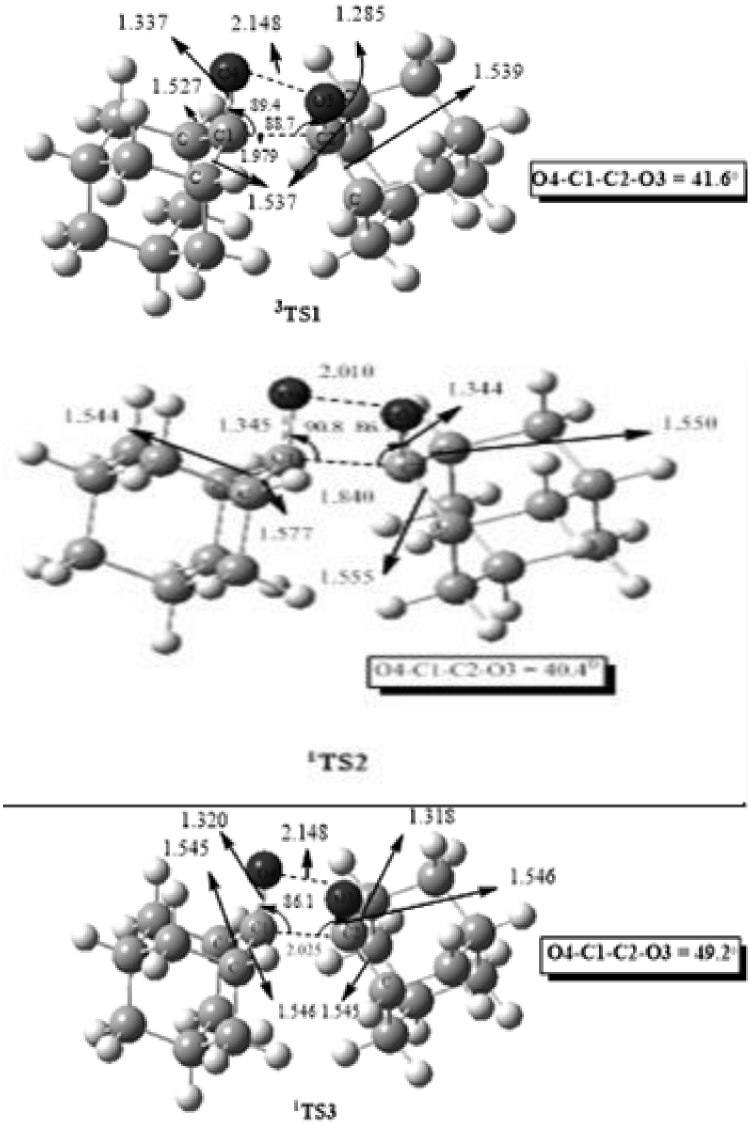
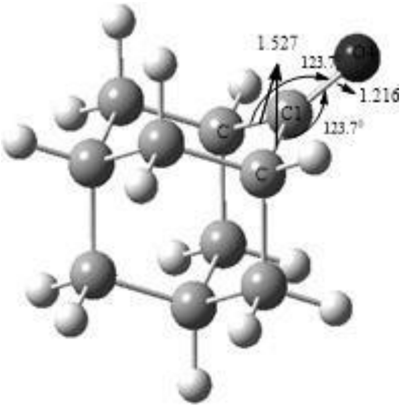


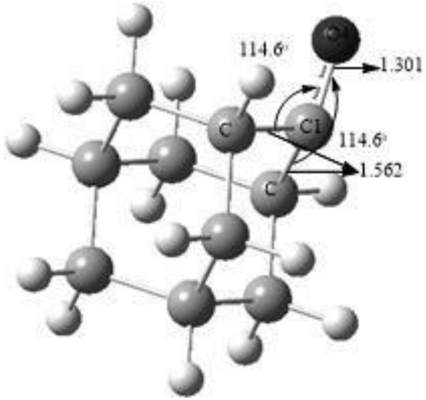
Figure 2. Optimized geometrical parameters of the dioxetane ring in the ^{1}TS1, ^{3}BR, ^{1}TS2 and ^{3}TS1 and ^{1}TS3 of BAAD. Bond length in Ǻ, bond angle and dihedral angle in degrees.

Table 3: Total Energies of 2-Adamantanone (AD) and Formaldehyde (FL); B3LYP/6-31G* for S_0 and UB3LYP/6-31G* for T_1 states.

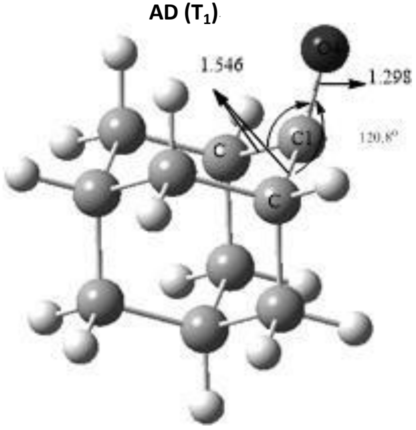
Products	**Energy (Hartree)**	**Relative Energy (kcal/mol)**
AD(S_0) + AD(S_0)	-929.4732772	-71.17
AD*(T_1) + AD(S_0)	-929.3580991	-1.17
AD(S_0) + AD*(S_1)^a	-929.3321253	17.41
AD*(T_1) + AD*(T_1)	-929.242921	73.34
AD (S_0) + FL (S_0)	-579.2454792	-60.62
AD (S_0) + FL*(T_1)	-579.1375203	7.13
FL (S_0) + AD*(T_1)	-579.1303011	11.66
AD*(T_1) + FL*(T_1)	-579.0223422	79.4
a: TD-B3LYP/6-31G* *: Excited state		



AD (S_0)



AD (T_1)



AD (S_1)

Figure 3. Geometrical structures of the adamantanone (AD) in S_0, T_1 and S_1 states.

CONCLUSION

Unlike the other systems, it is observed that the mechanism of the chemiluminescent decomposition of AAD prefers a concerted pathway *via* the transition state ^{1}TS3 in the singlet excited state with a lower activation barrier of 24.8 kcal/mol. The step-wise biradical pathway possesses a higher activation barrier of 29.1 kcal/mol. The analysis reveals different mechanisms for the chemifluorescent and chemiphosphorescent in AAD. The results are in agreement with the earlier experimental study.

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