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Density functional theory study of benzoic acid decarboxylation

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ABSTRACT

Mechanism of decarboxylation reaction includes, metal catalyst with Ag^+, a radical path and oxidative decarboxylation have been investigated. The calculations have been done in two different B3LYP/LANL2DZ, and WB97XD/DGDZVP/ DEF2DTZV levels. Four structures have been proposed for oxidized benzoic acid. Among four possible oxidative structures only one structure with 62.99 kcal.mol^{-1} activation energy could lead to the decarboxylative product. Silver catalyzed decarboxylation leads to products in one step. The activation energy for this path have been determined to be 43.31 kcal.mol^{-1}. The radical path for decarboxylation needs 16.93 kcal.mol^{-1} although for radical creation it needs at least 100.12 kcal.mol^{-1} energy.
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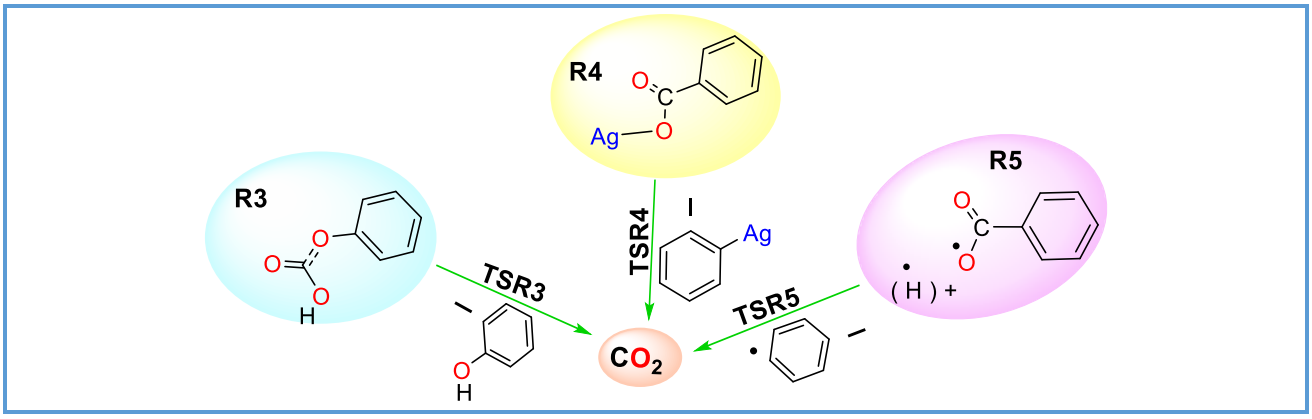
Graphical Abstract



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Introduction

Decarboxylation of benzoic acids is one of the important reactions for synthesis of C-H bond, C-C bond and C-X bond formation. These reactions have received considerable attention during the past years. The carboxylic acid functional group on the benzene ring can be considered to be an appropriate group for the replacement. The decarboxylation reaction is used for coupling reactions such as intramolecular direct arylation of Fluoren-9-one derivatives [1], heck reaction [2], cross coupling reaction [3] and decarboxylative C–H cross-coupling reactions [4]. Decarboxylation would lead to other kinds of bond formation such as conjugate addition reaction [5], C-S bounding formation [6] and amination [7] Transition metals such as palladium [8], silver [9], gold [10], nickel [11], rhodium [12] and copper [13] have been used for the decarboxylation of benzoic Decarboxylation acids. Decarboxylation reaction procedures with transition metal catalysts have been investigated wildly and there are many reports in literature about them. However, there are only countable protocols for the oxidative decarboxylation of aryl carboxylic acids under transition-metal-free conditions. Metal free methods such as the use of strong acids [14], enzymes[15], DBU as organocatalysts [16] and (Diacetoxyiodo)benzene/NaN_3 [17] have been reported for Decarboxylation of aromatic acids.

Among the first literature in the mechanism of decarboxylation, Cohen and Schambach have proposed a mechanism for copper(I) catalyzed oxidative decarboxylation, which involves copper ion forming a π-complex with aromatic rings of benzoic acids which caused formation of carbanion [18]. Anderson and Kochi studied kinetic of decarboxylation and proposed a radical mechanism for decarboxylation with metal ions, which initiates with the carboxylate radical formation [19]. Zhang and et al. investigated mechanism of Pd-catalyzed decarboxylative coupling with olefins. They report that decarboxylation occurs in a dissociative reaction path to produce a Pd (II)-aryl product [20]. Xue and et al., proposed a reaction path starting with an O-coordinate carboxylate complex [21].

In this work, we investigated mechanism of three different methods of decarboxylation reactions, oxidative decarboxylation (path A), Ag catalyzed decarboxylation (path B) and radical path (path C). Three different calculation methods B3LYP/LANL2DZ, WB97XD/ DGDZVP/DEF2DTZV and B3LYP/aug-ccVDZ, have been used for path A and C. Path B have been calculated with B3LYP/LANL2DZ and WB97XD/DGDZVP/DEF2TZV methods.

Experimental

Computational methods

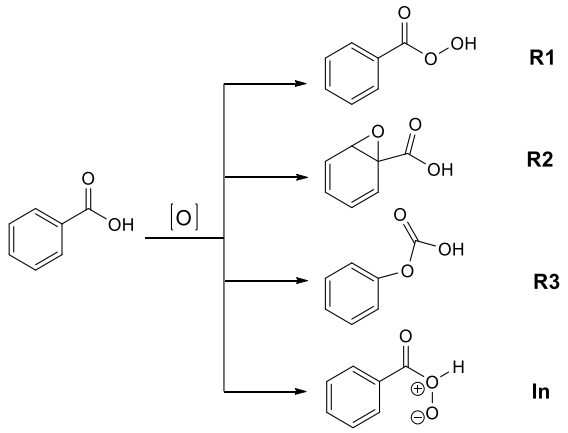
The Gaussian 09 [22] was employed to perform quantum-chemical calculations. The geometries for all the species including the reactants, products and the transition states were optimized by using the density functional (DFT) method [23-25]. The DFT/B3LYP method LANL2DZ basis set [26] and DFT/WB97XD method by DGDZVP basis set and DEF2TZV fitting set was employed for the relativistic effects in the Ag atom. The DFT/B3LYP method, aug-ccVDZ basis set was employed for non-metal structures. Vibrational frequency analyses were performed using the same level of theory to obtain the zero-point energies (ZPE) and identify all of the stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency) on the potential energy surfaces (PES). All the reported energies were corrected for the zero point vibrational energies (ZPVE). In addition,

the intrinsic reaction coordinates (IRC) calculations [27] were carried out to confirm that the identified transition states connect with reactants and products. All calculations were performed under the condition of 298.15 K and 0.1 MPa. In this paper, for all of the figures that contain potential energy profiles, relative free energies (kcal.mol^{-1}) and Zero-point energy (kcal.mol^{-1}) have been calculated.

Results and Discussion

Oxidative decarboxylation reaction

The various structures that may result from the oxidation of benzoic acid are shown in Scheme 1. The oxidized benzoic acid can exist as three forms: peroxy acid (**R1**), arene oxide (**R2**) and hydrogen carbonate (**R3**). The potential energy surfaces for decarboxylation of oxidized benzoic acid from **R1**, **R2**, and **R3** are depicted in Figure 1, from which it is clear that the peroxide form is lower in Gibbs energy than the other forms. The Geometry optimization structures calculated for path A are shown in Scheme 2. Bond, angel and dihedral parameters of **R1**, **R2, R3**, transition state (**TSR1**) for conversion of **R1** to intermediate (**In)**, transition state for conversion of **In** to **R2** (**TSIn**), transition state (**TSR2**) for conversion of **R2** to **R3** and transition state (**TSR3**) are listed in Table 1. **R3** decarboxylation to **P1** is performed in one step. This transformation proceeds via **TSR3**, in this conversion the C_4-O_9 bond is broken and simultaneously, the new single bond between O_9 and C_4 carbon atoms is formed. This is accompanied with an increase of Gibbs free energy by about 62 kcal.mol^{-1} Decarboxylation of **R2** to **P1** is not possible in one step. In this transformation, **R2** converted to **R3**. The energy barrier for this transformation is about 43 kcal.mol^{-1}. In the last step, decarboxylation is achieved through **R3** to **P1** pathway. Decarboxylation starting from peroxybenzoic acid has a path with three-steps. The first step is an hydride shift between O9 and O15 that leads to **In**. This conversion proceed from **TSR1** with energy of 62 kcal.mol^{-1}. Conversion of **In** into **R2** proceeds via insertion of oxygen O9 in to C=C bond. In this transformation, the reaction system passes from transition state **TSIn** with gibbs free energy by about 40 kcal.mol^{-1}. However, intermediate **In** may be the first material produced in the oxidation process of benzoic acid. Three different calculation methods B3LYP/LANL2DZ, WB97XD/ DGDZVP/DEF2DTZV and B3LYP/aug-ccVDZ have been used for calculating of energy for oxidative decarboxylation Table 2. As results show except for TSR1, in DFT/B3LYP/LANL2DZ method have the best results with lowest TS energies.



Scheme 1. Proposed structures for oxidation of benzoic acid

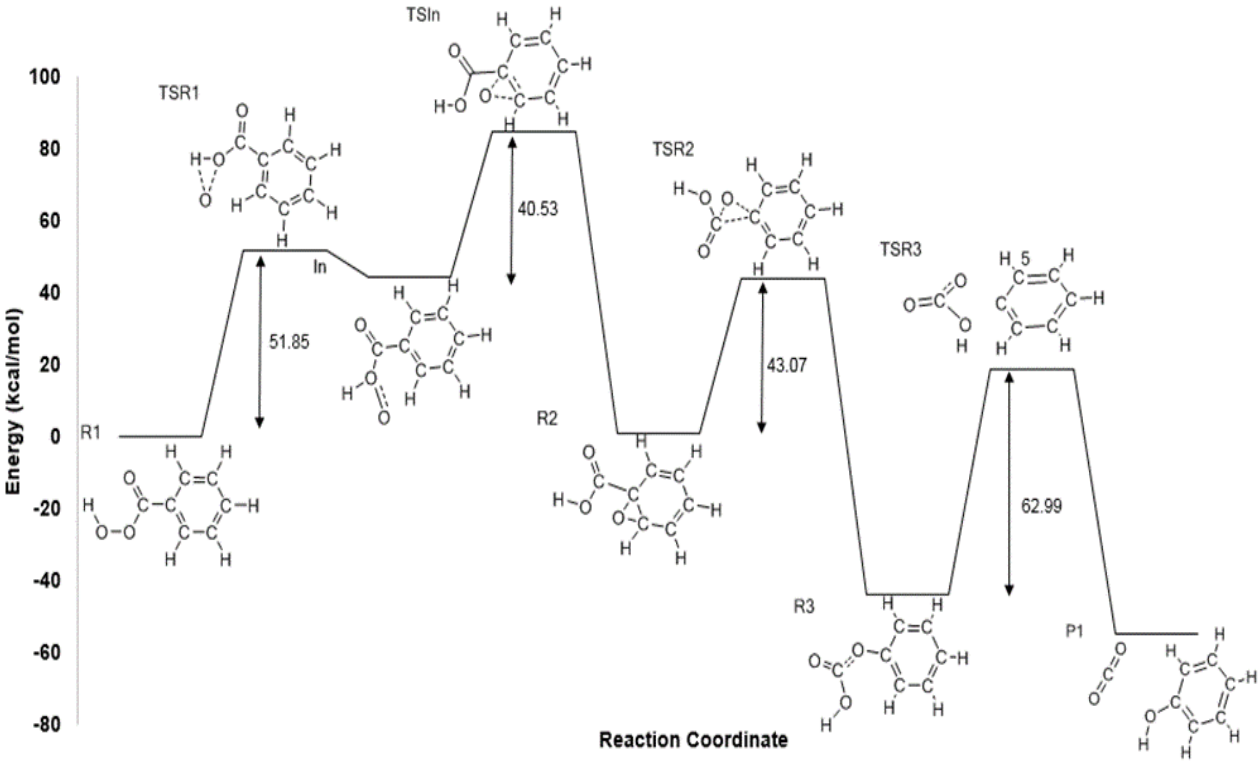
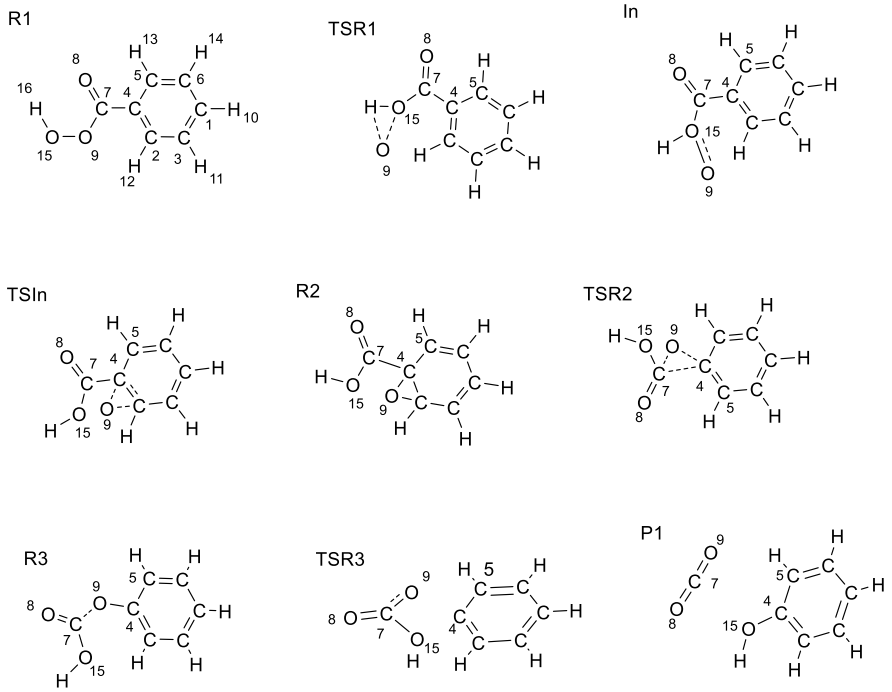


Figure 1. Reaction coordinate for path A



Scheme 2. Calculated structures for path A

Silver benzoate decarboxylation

The decarboxylation of silver benzoate (path B) takes place in one step Figure 2. In path B conversion of R4 to P2 from TSR4 have relative potential energy barrier about 43 kcal.mol^{-1}. Geometry optimization structures of silver benzoate R4, transition states TSR4, and the product complex P2 are shown in Scheme 3. Bond, angel and dihedral parameters of R4, TSR4, and P2 are listed in Table 3.

DFT/B3LYP method by using LANL2DZ basis set and WB97XD method by DGDZVP basis set and DEF2TZV fitting set have been used for calculating energy path B Table 4. There are relatively good matching between two method results.

Table 1. Optimized structures parameters for path A, with DFT/B3LYP/ LANL2DZ method

Entry	Zero Point energy (au)	Bond Length ArC_4-C_7 (Å)	Angle O_8-C_7-O_9	Dihedral C_5-C_4-C_7-O_9
R1	-495.76	1.466	120.315	179.940
TSR1	-495.68	1.468	116.802	-155.752
In	-495.69	1.463	132.120	-158.712
TSIn	-495.63	1.473	123.765	-119.688
R2	-495.76	1.481	-	-
TSR2	-495.69	1.547	116.742	-101.256
R3	-495.83	2.507	123.583	-91.427
TSR3	-495.73	2.385	141.383	-87.265
P1	-495.85	3.664	176.030	0.001

Table 2. Relative energy (Kcal.mol^{-1}) for path A

Method	R1	TSR1	In	TSIn	R2	TSR2	R3	TSR3	P1
B3LYP/LANL2DZ	0.0	51.85	44.25	84.78	0.93	43.99	-44.02	18.98	-54.68
WB97XD/DGDZVP/ DEF2DTZV	0.0	52.78	58.38	90.55	-15.61	41.60	-57.63	9.17	-67.68
B3LYP/aug-ccVDZ	0.0	51.21	58.86	89.11	-9.78	38.57	-53.51	8.66	-66.55

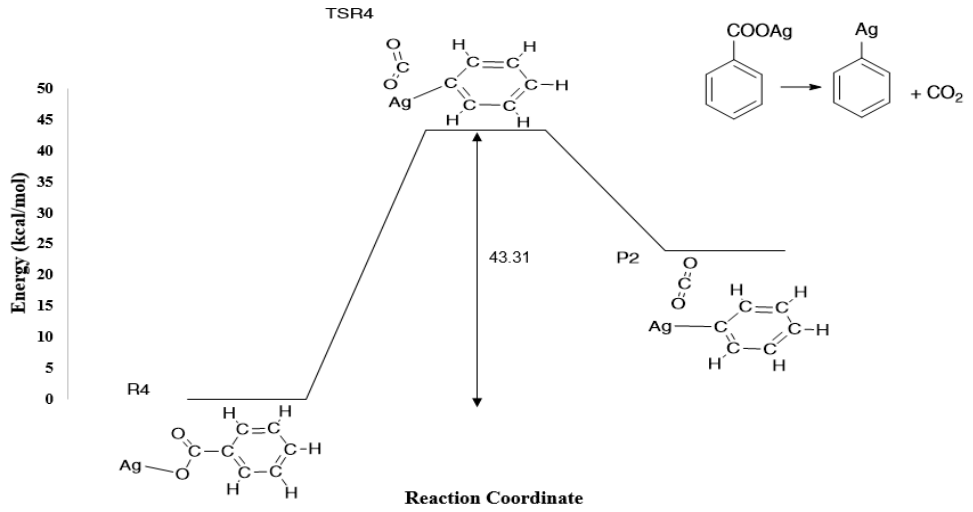
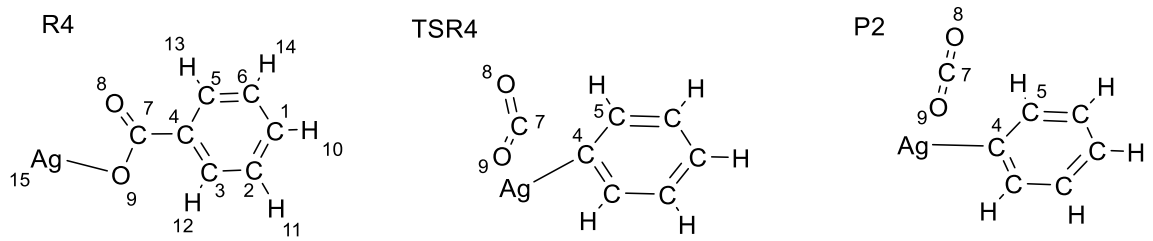


Figure 2. Reaction coordinate for path B



Scheme 3. Calculated structures for path B

Table 3. Optimized structures parameters for path B, with DFT/B3LYP/ LANL2DZ method

Entry	Zero Point energy (au)	Bound Length ArC_4-C_7 (Å)	Angle O_8-C_7-O_9	Dihedral C_5-C_4-C_7-O_9
R4	-565.84	1.4953	121.066	-179.995
TSR4	-565.77	2.0155	145.285	-160.385
P2	-565.80	3.579	178.924	-149.922

Table 4. Relative energy (Kcal.mol^{-1}) for path B

Method	R4	Tsr4	P2
B3LYP/LANL2DZ	0.00	43.31	23.93
WB97XD/DGDZVP/DEF2DTZV	0.00	43.47	28.16

Radical decarboxylation

Radical decarboxylation (path C) is performed in one step. The calculated reaction pathway is shown in Figure 3. In path C conversion of **R5** to **P3** from **TSR5** have relative potential energy barrier about 16.9 kcal.mol^{-1}. Before decarboxylation, the benzoic acid must be converted into the benzoate and hydrogen radicals (**R5**). Even without considering activation energy, this conversion requires about 100 kcal.mol^{-1}. The singlet multiplicity are considered for **R1**, **R5**, **TSR5** and **P3**.

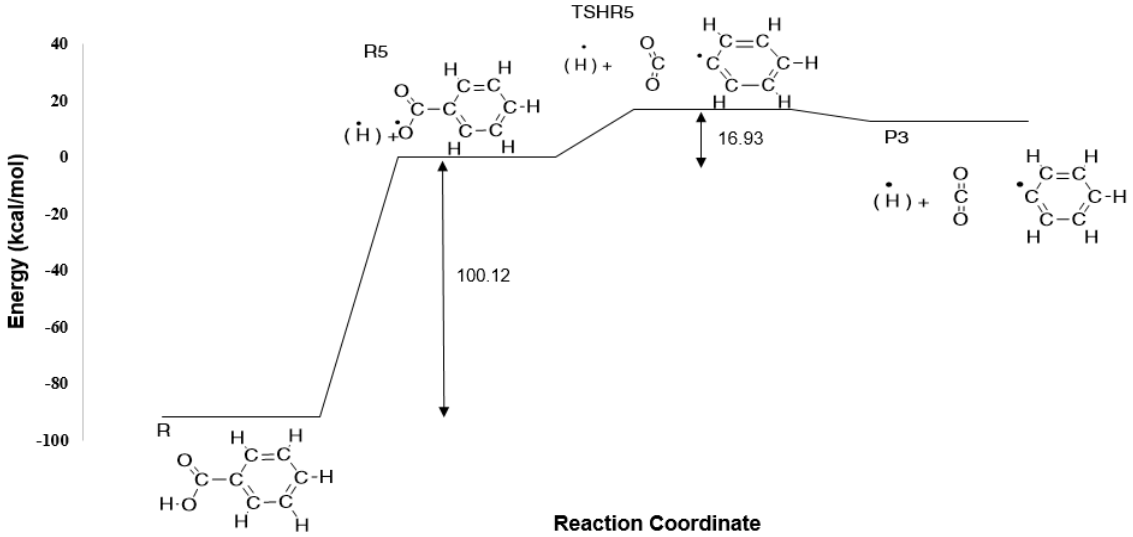
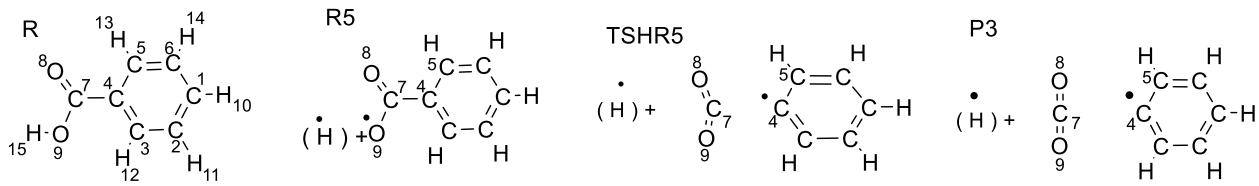


Figure 3. Reaction coordinate for path C



Scheme 4. Calculated structures for path C

Table 5. Optimized parameters of R, R5, TsR5 and P3 calculated with DFT/B3LYP method by using LANL2DZ basis set

Entry	Zero Point energy (au)	Bound Length ArC_4-C_7 (Å)	Angle O_8-C_7-O_9	Dihedral C_5-C_4-C_7-O_9
R	-420.65	1.484	121.095	180.000
R5	-419.99	1.472	110.850	179.988
TSR5	-419.97	2.114	156.606	179.560
P3	-419.97	3.069	178.318	-179.805
H radical	-0.5011	1.481	-	-

Table 6. Relative energy (Kcal.mol^{-1}) for path C

Method	R5	Tsr5	P3
B3LYP/LANL2DZ	0.00	16.93	12.79
B3LYP/DGDZVP /DEF2DTZV	0.00	10.07	1.79
DFT/B3LYP/aug-ccVDZ	0.00	9.54	1.45

Geometry optimization structures of benzoate radical **R5**, transition states **TSR5**, and product complex **P3** are shown in Scheme 4, DFT/B3LYP method by using LANL2DZ basis set, aug cc-pdvz basis set and WB97XD method by DGDZVP basis set and DEF2TZV fitting set have been used for calculating TS energy for radical condition, results for this calculation summarize in Table 5. As results shows cc-VDZ have the lowest TS energies. The relative energy of path C is shown in the Table 6.

Conclusions

Three different methods of benzoic acid decarboxylation reactio were studied. In this study, 3 products have been suggested for oxidation of benzoic acid. Among these oxidized structures, only one structure leads directly to the product with 62.99 kcal.mol^{-1}. Silver catalyzed decarboxylation leads to product with one step path. The activation parameters for this path have been determined as 43.31 kcal.mol^{-1}. The radical path needs 16.93 kcal.mol^{-1} activation energy. However radical production requires 100 kcal.mol^{-1}, which it is a limitation. B3LYP method was used to find transition states and calculate the reaction pathways using of LANL2DZ basis set which shows the best result compare to WB97XD/DGDZVP /DEF2TZV and B3LYP/aug-cc-pVDZ.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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