Theoretical Study on Mechanism of C₅H₇·+O₂ Reaction

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The potential energy surface (PES) for the reaction of E,E-pentadienyl with molecular oxygen was theoretically studied at the G3B3//B3LYP/6-311G(d,p) level of theory. The first step of the reaction was found to be the direct addition of molecular O₂ to either the C1 or the C3 atoms of E,E-pentadienyl, forming two C₅H₇O₂· isomers. These two C₅H₇O₂· isomers undergo a series of isomerization processes through either the hydrogen-transfer or cyclization pathway. In the final step, the hydrogen-transferred and cyclized isomers decompose into unsaturated aldehydes, unsaturated ketones, and hydroxyl radicals. Involves 20 stable species and 14 transition states, and the energies and structures of all reactants, products and transition states were calculated. Based on the calculated barriers and heats of formation, the authors suggest that the C₂H₃O→C₃H₅O formation channel is the dominant channel for the C₅H₇·+O₂ reaction. The possible existence of C₅H₅O₂· radicals as long lifetime intermediates is also proposed, which is consistent with the recent photoionization mass spectrometric experiments by Zils et al.

Key words: Pentadienyl, Oxygen, ab initio, Potential surface energy.

I. INTRODUCTION

The reactions of hydrocarbons with molecular oxygen have been a subject of intensive studies for several decades. Interest in these reactions has been motivated by their key role in atmospheric chemistry, low-temperature hydrocarbon oxidation, and autoignition processes. It has been well-recognized that polyenes are important intermediates in the combustion of benzene and polycyclic aromatic hydrocarbons (PAHs), and, accordingly, their reactions with molecular oxygen have received much attention [1-7]. Using photoionization mass spectroscopy, Ruiz et al. directly detected the existence of allylperoxy radicals in the C₅H₅·+O₂ gas-phase reaction [8]. With similar methods, Slagle et al. and Fenter et al. studied the reactions of several other hydrocarbon radicals (CH₃·, C₂H₅·, t-C₃H₇·, t-C₄H₉·, and benzyl) with O₂ [9-12]. Quech et al. theoretically studied the mechanism of C₂H₅·+O₂ reaction using ab initio method and proposed that the intramolecular hydrogen transfer pathway is the main process [13]. On the other hand, DeSain et al. suggested an epoxide formation mechanism for the reaction of propyl radical with molecular oxygen based on their theoretical calculations [14]. Mebel et al. studied the overall potential energy surface of the C₅H₃·+O₂ reaction using ab initio and RRKM calculations [15]. Recently, Taatjes et al. studied the reaction mechanisms of several alkyl radicals with molecular oxygen via a combination of new experimental measurements using the pulsed photolytically initiated oxidation reaction and state-of-the-art computational kinetics using ab initio calculations [16].

Despite of these experimental and theoretical efforts, the reactions of molecular oxygen with unsaturated hydrocarbon radicals have not been well-studied.

Recently, Zils et al. experimentally studied the reaction of the pentadienyl (C₅H₇·) radical with the molecular oxygen using a combination of pulsed laser photolysis and photoionization mass spectrometry [17]. In their experiments, the existence of the pentadienylperoxy (C₅H₇O₂·) radicals was detected, and the interconversion of different C₅H₇O₂· isomers was proposed. However, the mechanism and the molecular oxygen pentadienyl reaction has not been fully understood. For instance, the details of C₅H₅O₂· isomerization and the final products of the whole reaction are still unclear. In principal, the recently developed state-of-the-art quantum chemistry methods are capable of providing accurate results for molecular structures and chemical reactions [18-22]. In the present work, high-level ab initio molecular orbital methods are used to investigate the reaction between E,E-pentadienyl and O₂. The energies and structures of reactants, products and transition states were calculated and compared. Based on the calculated results, the mechanism of C₅H₇·+O₂ reaction is discussed.

II. COMPUTATIONAL DETAILS

Geometry optimizations for the stable structures and transition states of the C₅H₇·+O₂ reaction have been carried out with DFT methods using Becker’s three-parameter hybrid functional (referred as B3LYP) [23,24] and the standard 6-311G(d,p) basis sets. In the current work, frequency calculations in the optimized structures were performed using the same methods to estimate the zero-point energy corrections and to identify whether the obtained structures are sta-
able structures (without imaginary frequency) or transition states (with sole imaginary frequency). In order to obtain accurate energies for the key points of the potential energy surface (PES), single point energy calculations using the high level G3B3 method were carried out for all species. The G3B3 method is a variation of G3 (Gaussian-3) theory in which the geometries and zero-point energies are obtained from B3LYP density functional theory. For the G3B3 method, the MP4(FC))/6-31G(d), MP4(FC)/6-31+G(d), MP4(FC)/6-31G(2df,p) QCISD(T,FC)/6-31G(d), and MP4(FU)/G3 large calculations are carried out and formulated to obtain accurate single-point energies. Spin-orbital (SO) correction and high-level correction (HLC) are also included. The details of G3B3 theory have been described in literature [25,26] and will not be presented here. The G3B3 average absolute deviation from the 299 experimental energies for the G2/97 test set is 4.14 kJ/mol, which shows a slight improvement in comparison with the 4.22 kJ/mol average absolute deviation for G3 theory [26]. It has been demonstrated that the G3B3 method can provide accurate absolute deviation for G3 theory [26].

It has been suggested that the pentadienyl radicals (C5H7·) can exist as either the E,E or the E,Z conformation [35-38].

G3B3/B3LYP calculations were conducted for both conformations and it was found that the energy of E,E-pentadienyl is lower by 9.2 kJ/mol than that of E,Z-pentadienyl. Therefore, the present study was concentrated on the reaction of molecular oxygen with the E,E-pentadienyl radical. Figure 1 shows the optimized geometries of all stable structures and transition states. Based on the G3B3/B3LYP/6-311G(d,p) calculations, the overall potential energy surface of the reactions is depicted in Fig.2. The relative energies at 0 K with ZPE corrections of all reactants, products and transition states are compiled in Table I, and the ZPE corrections are based on the G3B3 computed values with the default scale factor of Gaussian03. The vibrational frequencies calculated with B3LYP/6-311G(d,p) are listed in the Table II for the reactants, products and transition states of the dominant channel.

A. The formation of C2H-O2- adducts

According to these calculations, the C5H6 radical can directly react with the ground state O2 (triplet state) to produce two O2-adducts: ISO1 (CH2CHCHCHCH2OO·) (“·” denotes an unpaired single electron) and ISO2 (CH2CHCH(OO·)CHCH2), through the following reactions:

\[
\begin{align*}
\text{CH}_2\text{CHCHCHCH}_2 + \text{O}_2 & \rightarrow \text{TS1} \rightarrow \text{ISO1} \quad (1) \\
\text{CH}_2\text{CHCHCHCH}_2 + \text{O}_2 & \rightarrow \text{TS2} \rightarrow \text{ISO2} \quad (2)
\end{align*}
\]

ISO1 is formed by the addition of O2 molecule onto the terminal carbon (C1 atom) of the C5H7· radical, whereas ISO2 is formed by the addition of O2 molecule onto the middle carbon (C3 atom). According to the G3B3 calculations, the energy of the ISO1 is lower than that of the reactants by 55.2 kJ/mol, and the barrier of Reaction (1) is 44.7 kJ/mol. The energy of the ISO2 is 43.9 kJ/mol lower than that of the reactants, while the reaction barrier is 26.7 kJ/mol.

The O2-adduction changes the orbital hybridization of the attached carbon atom from sp2 to sp3 and thus destroys the π-conjugation of the original carbon chain of C5H7·. As a result, both ISO1 and ISO2 show significant non-planar distortion, in contrast to the E,E-pentadienyl radical that have all the atoms in the same plane. For ISO1, while the five carbon atoms are nearly coplanar due to the electronic conjugation of C2C3C4C5 chain, the two hydrogens on the C1 atom and the two oxygen atoms are tilted with respect to the C2C3C4C5 plane. For ISO2, the C1, C2, C4, C5 atoms are nearly in the same plane whereas the sp3 hybrid C3 atom is tilted from the C2C3C4C5 plane, showing that the C2=C3 and C4=C5 bonds of ISO2 exist as two isolated double bonds.

In the experimental work of Zils et al., the enthalpy change for the reaction C5H7·+O2→C5H7O2· was suggested to be ±6±5 kJ/mol deduced from the measured reaction rate constant [10]. It seems that the enthalpy change reported by Zils et al. is actually an averaged result for Reaction (1) and Reaction (2). According to the current calculations, the enthalpy changes for the Reaction (1) and Reaction (2) are 58.1 and 47.0 kJ/mol, respectively. Thus, we can consider these calculations to be quite consistent with the experiments.
FIG. 1 The optimized geometries of reactants, products, and transition states at the B3LYP/6-311G(d,p) level of theory for the reaction of 
E,E-pentadienyl with O$_2$. The bond length and angle are in Å and (°), respectively. (to be continued)
FIG. 1 Continued
Reaction Mechanism of \( \text{C}_5\text{H}_7 + \text{O}_2 \)  

B. Isomerization of \( \text{C}_5\text{H}_7\cdot\text{O}_2 \) adducts

The calculations demonstrated that the two \( \text{O}_2 \)-adducts, \( \text{CH}_2\text{CHCHCH}_2\text{OO} \cdot \) (ISO1) and \( \text{CH}_2\text{CHCH(OO} \cdot \text{)CHCH}_2 \) (ISO2), can undergo a series of isomerization processes, with either a hydrogen-transfer or a cyclization route.

1. Isomerization via hydrogen-transfer

Both ISO1 and ISO2 can undergo hydrogen-transfer isomerization:

\[
\begin{align*}
\text{ISO1} & \rightarrow \text{TS3} \rightarrow \text{ISO3} & \text{(3)} \\
\text{ISO1} & \rightarrow \text{TS4} \rightarrow \text{ISO4} & \text{(4)} \\
\text{ISO2} & \rightarrow \text{TS5} \rightarrow \text{ISO5} & \text{(5)} \\
\text{ISO2} & \rightarrow \text{TS6} \rightarrow \text{ISO6} & \text{(6)}
\end{align*}
\]

Reaction (3) is a \( \alpha \)-H transfer reaction in which the hydrogen atom on the C1 atom of ISO1 is extracted by the O7 atom that has an unpaired electron. This produces the isomer ISO3 via the transition state TS3. In addition to the \( \alpha \)-H transfer isomerization, the ISO1 can also undergo a \( \beta \)-H transfer reaction (Reaction (4)). In this reaction, the hydrogen atom on the C2 atom is extracted by the O7 atom, forming ISO4 through the transition state TS4.

ISO2 undergoes similar hydrogen-transfer process. In Reaction (5), the ISO5 is formed by transferring the hydrogen atom on the C3 atom to the O atom via the transition state TS5. In Reaction (6), ISO6 is produced from ISO2 through \( \beta \)-H transfer isomerization with TS6 as the transition state.

In comparison with the \( \beta \)-H transfer reactions, the \( \alpha \)-H transfer processes have lower barriers. For the ISO1 case, the \( \alpha \)-H transfer reaction (Reaction (3)) has a barrier of 168.4 kJ/mol, which is lower by 28.0 kJ/mol compared with the \( \beta \)-H transfer reaction (Reaction (4)). A similar tendency was observed in the H-transfer reactions of ISO2. The barrier of the \( \alpha \)-H shift reaction (Reaction(5)) is 162.2 kJ/mol, which is lower than that of

FIG. 2 Profile of potential energy surface for the reaction of \( E,E \)-pentadienyl with \( \text{O}_2 \). Relative energies (in kJ/mol) are calculated at the G3B3 level of theory.
TABLE I G3B3 calculated relative energies of reactants, products and transition states for the reaction of \(E,E\)-pentadienyl with \(O_2\)

<table>
<thead>
<tr>
<th>Species</th>
<th>(RE/(kJ/mol))</th>
<th>Species</th>
<th>(RE/(kJ/mol))</th>
<th>Imaginary frequency/cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_5H_7+O_2)</td>
<td>0.0</td>
<td>TS1</td>
<td>44.7</td>
<td>362i</td>
</tr>
<tr>
<td>ISO1</td>
<td>-55.2</td>
<td>TS2</td>
<td>26.7</td>
<td>273i</td>
</tr>
<tr>
<td>ISO2</td>
<td>-43.9</td>
<td>TS3</td>
<td>113.3</td>
<td>1718i</td>
</tr>
<tr>
<td>ISO3</td>
<td>-83.6</td>
<td>TS4</td>
<td>141.2</td>
<td>2110i</td>
</tr>
<tr>
<td>ISO4</td>
<td>47.2</td>
<td>TS5</td>
<td>118.3</td>
<td>1580i</td>
</tr>
<tr>
<td>ISO5</td>
<td>-82.8</td>
<td>TS6</td>
<td>126.6</td>
<td>2086i</td>
</tr>
<tr>
<td>ISO6</td>
<td>52.7</td>
<td>TS7</td>
<td>64.4</td>
<td>744i</td>
</tr>
<tr>
<td>ISO7</td>
<td>-13.8</td>
<td>TS8</td>
<td>105.7</td>
<td>889i</td>
</tr>
<tr>
<td>ISO8</td>
<td>-27.6</td>
<td>TS9</td>
<td>93.2</td>
<td>714i</td>
</tr>
<tr>
<td>ISO9</td>
<td>25.5</td>
<td>TS10</td>
<td>106.6</td>
<td>839i</td>
</tr>
<tr>
<td>ISO10</td>
<td>-142.9</td>
<td>TS11</td>
<td>138.3</td>
<td>681i</td>
</tr>
<tr>
<td>P1+OH</td>
<td>-185.2</td>
<td>TS12</td>
<td>56.4</td>
<td>604i</td>
</tr>
<tr>
<td>P2+OH</td>
<td>-176.8</td>
<td>TS13</td>
<td>70.6</td>
<td>621i</td>
</tr>
<tr>
<td>P3+OH</td>
<td>-48.9</td>
<td>TS14</td>
<td>89.4</td>
<td>824i</td>
</tr>
<tr>
<td>P4+CH(_2)O</td>
<td>-91.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_2H_3O+C_3H_4O)</td>
<td>-259.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE II The B3LYP/6-311G(d,p) calculated vibration frequencies of the reactants, products and transition states for the \(C_2H_3O+C_3H_4O\) formation channel of the reaction of \(E,E\)-pentadienyl with \(O_2\)

<table>
<thead>
<tr>
<th>Species</th>
<th>Frequencies/cm(^{-1})</th>
<th>Species</th>
<th>Frequencies/cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_5H_7)</td>
<td>158, 202, 257, 452, 491, 588, 629, 831, 843, 864, 929, 989, 1018, 1036, 1185, 1268, 1293, 1315, 1462, 1505, 1546, 1612, 3142, 3144, 3159, 3166, 3168, 3256, 3256</td>
<td>TS2</td>
<td>273i, 98, 119, 148, 200, 254, 294, 426, 481, 486, 628, 709, 908, 934, 947, 967, 1003, 1011, 1043, 1201, 1232, 1299, 1325, 1330, 1353, 1448, 1493, 1634, 1662, 3135, 3144, 3149, 3151, 3152, 3226, 3236</td>
</tr>
<tr>
<td>(O_2)</td>
<td>1641</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_2H_3O)</td>
<td>449, 505, 756, 974, 979, 1150, 1396, 1470, 1553, 2928, 3138, 3253</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_3H_4O)</td>
<td>171, 321, 572, 611, 919, 995, 1028, 1039, 1165, 1294, 1389, 1454, 1679, 1785, 2864, 3130, 3168, 3221</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Thus, the relative lower barriers for the \(\alpha\)-H transfer reactions compared with the \(\beta\)-H transfer reactions are probably due to their shorter distances between the H-donor and H-acceptor.

The heats of formation for the \(\alpha\)-H transfer Reactions (3) and (5) were calculated to be 27.6 and 38.9 kJ/mol, respectively, indicating that the \(\alpha\)-H transfer reactions are exothermic. On the contrary, the heats of formation for the \(\beta\)-H transfer reactions (Reactions

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Cyclization pathways were also studied for the ISO1 and ISO2. Cyclized isomerization on the other hand, do not form a conjugated system. The products of α-H transfer reactions, the products (ISO3 and ISO5) have an unpaired electron on the C3 atom. This permits the five carbon atoms to form a conjugated system, which is expected to greatly decrease the energy of the system. The products of β-H transfer reactions (ISO4 and ISO6), on the other hand, do not form a conjugated system.

2. Cyclized isomerization

In addition to the hydrogen-transfer pathways, four cyclization pathways were also studied for the ISO1 and ISO2 isomerization:

\[
\begin{align*}
\text{ISO1} & \rightarrow \text{TS7} \rightarrow \text{ISO7} \quad (7) \\
\text{ISO1} & \rightarrow \text{TS8} \rightarrow \text{ISO8} \quad (8) \\
\text{ISO2} & \rightarrow \text{TS9} \rightarrow \text{ISO9} \quad (9) \\
\text{ISO2} & \rightarrow \text{TS10} \rightarrow \text{ISO8} \quad (10)
\end{align*}
\]

Reactions (7) and (9) are four-member-ring formation reactions for ISO1 and ISO2 respectively. Reaction (7) produces ISO7 that contains a C2C1O6O7 four-member-ring and leaves an unpaired electron on the C3 atom, whereas Reaction (9) produces ISO9 that contains a C2C3O6O7 four-member-ring and leaves an unpaired electron on the C1 atom. As the C5C4C3 chain in ISO7 forms a three-center-three-electron conjugated system, the energy of ISO7 is slightly lower than that of ISO9 by 39.3 kJ/mol. Reactions (8) and (10) are five-member-ring formation reactions for ISO1 and ISO2 respectively, which lead to the same product ISO8 with a C3C2C1O6O7 five-member-ring. The C3, C2, O6, O7 atoms in ISO8 are nearly coplanar, while its C1 atom is clearly out of the C3C2O6O7 plane.

These calculations indicate that the five-member-ring formation reactions have higher barriers than the four-member-ring formation reactions. For the ISO1 case, the four-member-ring formation reaction (Reaction (7)) has a barrier of 119.5 kJ/mol, which is 41.4 kJ/mol lower than the five-member-ring formation reaction (Reaction (8)). Consistent with this, for the ISO2 case, the barrier of the four-member-ring formation reaction (Reaction (9)) is 13.4 kJ/mol lower than the five-member-ring formation reaction (Reaction (10)). This tells us that the five-member-ring formation processes require a large distortion for the carbon frameworks whereas the four-member-ring formation processes require only small distortion for the carbon frameworks. Therefore we suggest that the large distortion of carbon framework is responsible for the higher barrier of five-member-ring formation reactions.

Although the five-member-ring formation reactions are kinetically unfavorable, the relative energies of their products are lower than those of four-member-ring formation reactions. In the ISO1 pathways, the energy of ISO8 (the product of Reaction (8)) is 27.6 kJ/mol higher than ISO1, while the energy of ISO7 (the product of Reaction (7)) is 41.4 kJ/mol higher than ISO1. In the ISO2 pathways, the product of Reaction (10) is higher than the reactant by 16.3 kJ/mol, while the product of Reaction (9) is higher by 69.4 kJ/mol. In view of the structural difference between the cyclic products, we suggest that the greater strain of the four-member-ring than the five-member-ring is responsible for the smaller heats of formation for the corresponding reactions.

C. Unimolecular decomposition of the C₅H₇O₂ isomers

Most hydrogen transferred isomers and cyclized isomers undergo unimolecular decomposition pathways. The primary products are either the unsaturated aldehydes or the unsaturated ketones:

\[
\begin{align*}
\text{ISO3} & \rightarrow \text{P1} + \text{OH} \quad (11) \\
\text{ISO5} & \rightarrow \text{P2} + \text{OH} \quad (12) \\
\text{ISO4} & \rightarrow \text{TS11} \rightarrow \text{P3} + \text{OH} \quad (13) \\
\text{ISO8} & \rightarrow \text{TS12} \rightarrow \text{ISO10} \rightarrow \text{P4} + \text{CH₂O} \quad (14) \\
\text{ISO7} & \rightarrow \text{TS13} \rightarrow \text{ISO10} \rightarrow \text{P4} + \text{CH₂O} \quad (15) \\
\text{ISO9} & \rightarrow \text{TS14} \rightarrow \text{C₂H₃O}· + \text{C₃H₄O} \quad (16)
\end{align*}
\]

Reaction (11) and Reaction (12) are the unimolecular decomposition of the α-H transferred isomers ISO3 and ISO5, respectively. The calculations indicate that these two reactions can take place directly without any barrier. The products of Reaction (11) are hydroxyl and P1 (an unsaturated aldehyde), and the heat of formation for this reaction is 101.6 kJ/mol. Similarly, the products of Reaction (12) are hydroxyl and P2 (an unsaturated ketone). The slight difference between the products of the two reactions is due to the difference positions of the O atom in ISO3 and ISO5. For the β-H transferred isomers, the ISO4 decomposes to P3 (a radical with a three-member-ring structure) and hydroxyl via the transition state TS11 (Reaction (13)). The barrier and the heat of formation of Reaction (13) are 91.1 and 96.1 kJ/mol, respectively.

Decomposition reactions were also found for the cyclized isomers ISO7, ISO8, and ISO9. For the five-member-ring isomer ISO8, Reaction (14) indicates that it decomposes to P4 (a radical with a three-member-ring structure) and formaldehyde with TS12 as the transition state and ISO10 as the intermediate. The barrier and the heat of formation of Reaction (14) are 84.0 and 63.9 kJ/mol, respectively. In addition to the ISO8 decomposition channel, P4 and formaldehyde can also be produced from the four-member-ring isomer ISO7 by Reaction (15). In Reaction (15), ISO7 isomerizes to ISO10 firstly through the transition state TS13.
Then, ISO10 directly decomposes to P4 and formaldehyde by cleaving the C1–C2 bond. The barrier and the heat of formation of Reaction (15) are 84.4 and 77.7 kJ/mol, respectively. In another four-member-ring isomer decomposition pathway Reaction (16), ISO9 decomposes to acraldehyde and C2H4O through the transition state TS14. The barrier of Reaction (16) is 63.9 kJ/mol and the heat of formation is 285.1 kJ/mol.

According to the calculated potential energy surface, in the first step, Reaction (2) has a slightly lower barrier than that of Reaction (1) by 18.0 kJ/mol. Subsequently, the isomerization Reaction (9) has a barrier of 137.1 kJ/mol, which is lower than the barriers of most of the other isomerization reactions. In the final step, the decomposition of ISO9 has the lowest barrier, 63.9 kJ/mol, among all of the decompositions of C5H7O2-isomers, and the decomposition of ISO9 has a very large heat of formation (285.1 kJ/mol). Despite the fact that Reaction (7) (the isomerization of ISO1 to ISO7) has a slightly lower barrier than that of Reaction (9) by 17.5 kJ/mol, the barrier for the decomposition of ISO7 is higher than that of ISO9 by 20.1 kJ/mol, and the heat of formation for the decomposition of ISO9 is much smaller than that of the ISO9 by 207.3 kJ/mol. Therefore, the following C2H4O+→C3H5O formation channel is considered to be the dominant reaction channel for the C5H7+O2 reaction:

\[
\begin{align*}
\text{C}_5\text{H}_7 + \text{O}_2 & \rightarrow \text{TS}_2 \rightarrow \text{ISO}_2 \\
\text{ISO}_2 & \rightarrow \text{TS}_9 \rightarrow \text{ISO}_9 \\
\text{ISO}_9 & \rightarrow \text{TS}_{14} \rightarrow \text{C}_2\text{H}_3\text{O} + \cdot\text{C}_3\text{H}_4\text{O}
\end{align*}
\]

The total barrier of this channel is 93.2 kJ/mol, and the overall heat of formation for this channel is 259.6 kJ/mol. The barrier of Reaction (9) ISO2→TS9→ISO9 is the highest (137.1 kJ/mol), indicating that Reaction (9) is the rate-determining step for this channel. In addition, the present calculations demonstrate that several C5H7O2-isomers have relative low energies. In particular, the epoxidyl radical ISO10 has quite a large overall heat of formation (129.2 and 115.4 kJ/mol, relative to ISO7 and ISO8 respectively), a very high backward barrier (164.3 and 174.7 kJ/mol for TS12 and TS13, respectively), and an intermediate forward barrier (51.4 kJ/mol). Also, the O2-adduct ISO1 has an intermediate heat of formation (55.2 kJ/mol), and quite high forward and backward barriers (137.1-185.6 and 99.9 kJ/mol, respectively). We thus deduce that these species may exist with a lifetime long enough to be experimentally observed. This is consistent with the Zils’s experimental observation, from which the existence of C5H7O2 intermediates has been identified for the reaction of E,E-pentadienyl with molecular oxygen.

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