

Quantum chemical investigation of the reaction of $O(^3P_2)$ with certain hydrocarbon radicals

ASHUTOSH GUPTA,¹ R P SINGH,¹ V B SINGH,¹ BRIJESH KUMAR MISHRA³ and N SATHYAMURTHY^{3,*}

¹Department of Chemistry, ²Department of Physics, Udai Pratap Autonomous College, Varanasi 221 005

³Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208 016

e-mail: nsath@iitk.ac.in

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Abstract. The reaction of ground-state atomic oxygen [$O(^3P_2)$] with methyl, ethyl, *n*-propyl and iso-propyl radicals has been studied using the density functional method and the complete basis set model. The energies of the reactants, products, reaction intermediates and various transition states as well as the reaction enthalpies have been computed. The possible product channels and the reaction pathways are identified in each case. In the case of methyl radical the minimum energy reaction pathway leads to the products $CO + H_2 + H$. In the case of ethyl radical the most facile pathway leads to the products, methanal + CH_3 radical. For propyl radical (*n*- and *iso*-), the minimum energy reaction pathway would lead to the channel containing ethanal + methyl radical.

Keywords. Methyl radical; ethyl radical; propyl radical; triplet oxygen.

1. Introduction

Reactions of atomic oxygen with hydrocarbon radicals play an important role in understanding the mechanism of reactive elementary processes at the molecular level.¹ They provide important insights into combustion, hydrocarbon synthesis, interstellar reactions and atmospheric chemistry. Not much information on such radical reaction dynamics is available in comparison to the extensive theoretical and experimental studies on reaction of stable closed-shell molecules.² The scarcity of studies on such systems is mainly due to the experimental difficulties in generating clean radicals efficiently. Such drawbacks have been overcome by adopting the supersonic flash pyrolysis source developed in short-pulse experiments. Chen and co-workers pioneered the spectroscopic studies to characterize the electronic structure and unimolecular photodissociation of several hydrocarbon radicals.³ For bimolecular reactive scattering processes, only a few experimental studies have been reported in recent years. The exoergic reaction of ground-state atomic oxygen [$O(^3P_2)$] with vinyl radicals (C_2H_3) using arrested relaxation Fourier transform

infrared (FT-IR) spectroscopy and non-statistical vibrational distribution of the CO product was studied by Donaldson *et al*.⁴ The reaction of $O(^3P_2)$ with methyl radicals (CH_3) under low pressure flow conditions, manifesting an indirect addition mechanism was carried out by Bersohn and co-workers.⁵ One of the product channels was found to be $CO + H_2$ and H. The reaction of propargyl radical (C_3H_3) with ground-state atomic carbon [$C(^3P_2)$] in a crossed beam configuration was studied by Lee and co-workers⁶ using time-of-flight spectroscopy and measuring angular distribution of the product C_4H_2 .

Among the several hydrocarbon radicals studied so far, the reactivity of allyl radical (C_3H_5) has attracted much theoretical and photochemical attention.^{7,8} C_3H_5 is an intermediate in the pyrolysis of hydrocarbons and is important in tropospheric and stratospheric chemistry. It is one of the smallest π -conjugated systems stabilized by two equivalent resonance structures. Besides the allyl radical, propargyl radical (C_3H_3) has also been studied due to its being the simplest π -conjugated hydrocarbon radical with an odd number of electrons.⁹ Propargyl radical has been the focus of theoretical and experimental studies because of its role as the most important precursor to the formation of benzene and other polycyclic aromatic hydrocarbons in flames and as a central spe-

*For correspondence

cies producing vinylidenecarbene detected in the interstellar medium.¹⁰

The radical–radical dynamics of $O(^3P_2) + t\text{-C}_4\text{H}_9 \rightarrow \text{OH} + \text{iso-C}_4\text{H}_8$ under crossed beam conditions was studied by Choi and coworkers.¹¹ Density functional theoretic (DFT) calculations using the complete basis-set (CBS) have been carried out, with special attention to the reaction pathways and the major product channels. Their microscopic kinetics has been followed within the framework of Rice–Ramsperger–Kassel–Marcus (RRKM) theory.¹²

In the present work an attempt has been made to understand the radical–radical interaction of triplet oxygen atom $O(^3P_2)$ with small hydrocarbon radicals CH_3 , C_2H_5 and *n*- and *iso*- C_3H_7 . The motivation to the work lies in knowing the role of various hydrocarbon radicals reacting with oxygen atom particularly in interstellar space and in earth's atmosphere. An extensive search for various product channels, intermediates and transition states has been carried out using DFT method and complete basis set model (CBS-Q and CBS-QB3). An experimental study of the reaction of $O(^3P_2)$ with CH_3 radicals was reported by Min *et al*.¹³ They had detected the presence of CO in addition to the major product CH_2OH by laser induced fluorescence. There have also been reports on the reaction of C_2H_5 with O , O_3 and NO_3 by Hoyermann *et al*.¹⁴ The kinetics of the reaction between oxygen atoms and ethyl radicals was studied experimentally in a heatable tubular reaction vessel coupled to a photo-ionization mass spectrometer by Slagle *et al*.¹⁵ To the best of our knowledge, no other study of methyl, ethyl and propyl radical reactions with triplet oxygen has been carried out using hybrid DFT method and the complete basis set model.

2. Methodology

All the calculations were carried out using Gaussian 03 suite of programs.¹⁶ Various geometries (shown in figures 1–4) were optimized using DFT (B3LYP/6-311G(*d, p*)), CBS-Q and CBS-QB3 model.^{17–19} Vibrational frequencies were also computed to identify the stationary points and scaled by a factor of 0.98 for zero-point energy (ZPE) corrections. All the transition states were identified in terms of a single imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were carried out to make sure that the transition state connects to the designated reactants and products.

3. Results and discussion

The various channels proposed for the reaction of triplet oxygen atom with methyl, ethyl and *n*- and *iso*-propyl radicals are:

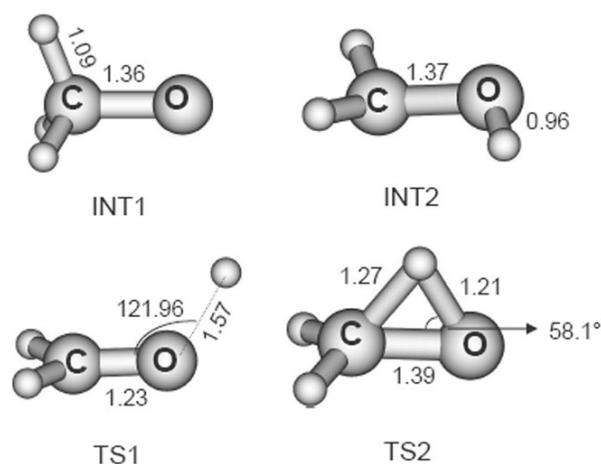
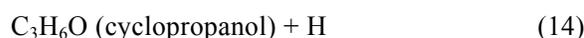
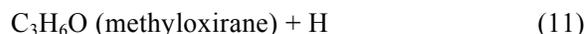
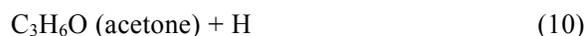
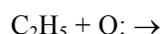
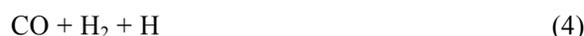
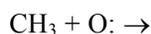


Figure 1. Optimized geometries of intermediates and transition states for the reaction of $O(^3P_2)$ atom with methyl radical at the CBS–QB3 level of theory. Distances are in Å.

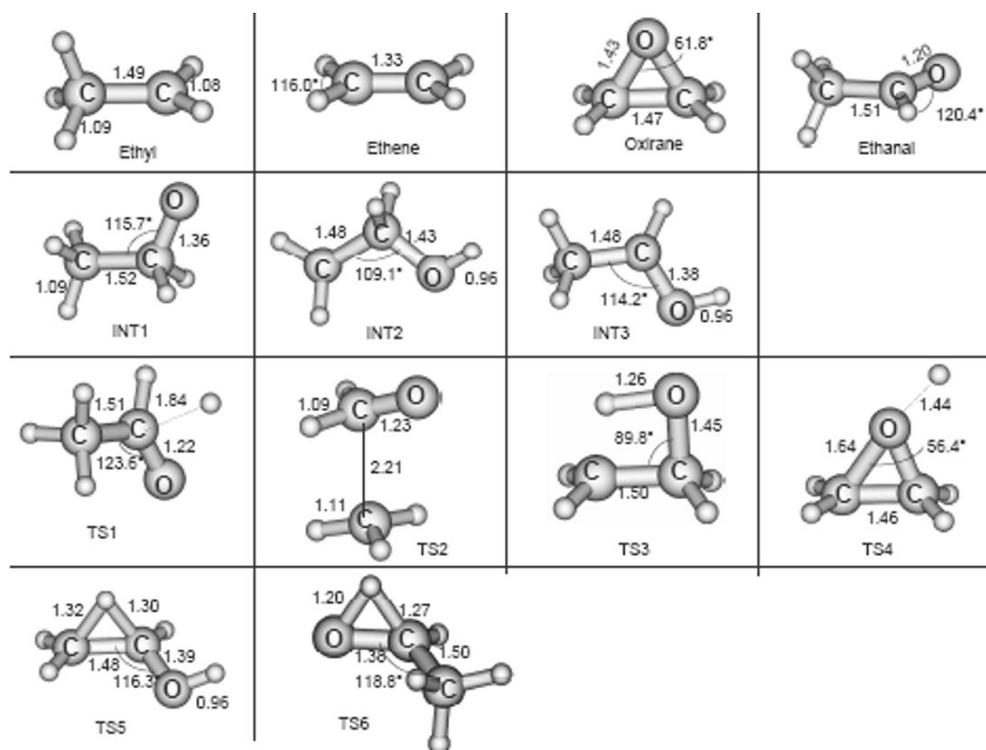


Figure 2. Optimized geometries of reactants, products, intermediates and transition states for the reaction of $O(^3P_2)$ atom with ethyl radical at the CBS-QB3 level of theory. Distances are in Å.

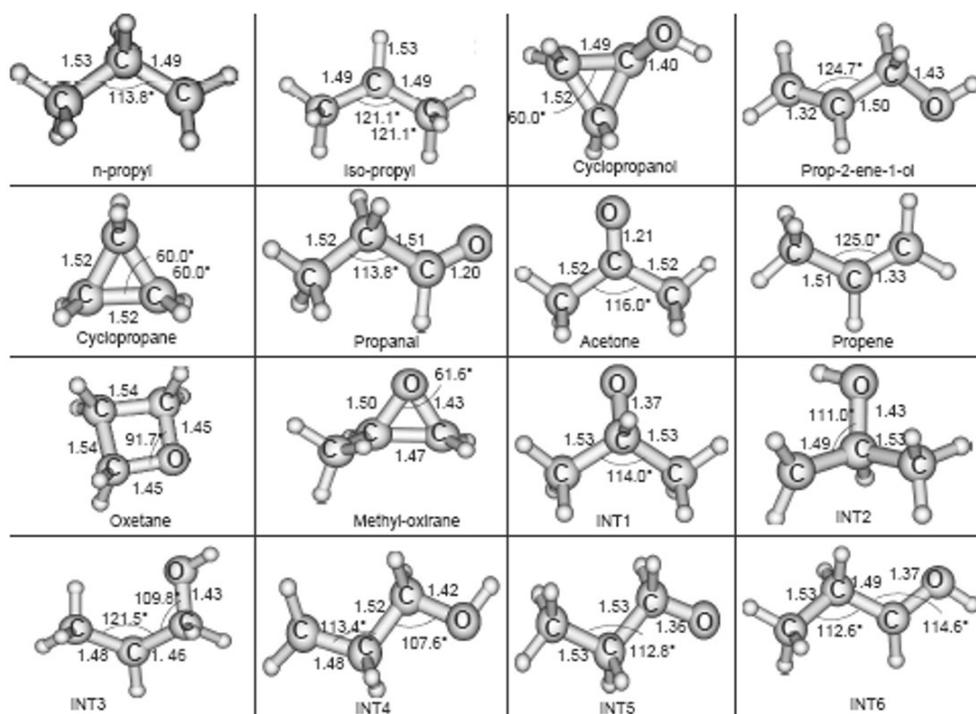


Figure 3. Optimized geometries of reactants, products and intermediates for the reaction of $O(^3P_2)$ atom with propyl radicals at the CBS-QB3 level of theory. Distances are in Å.

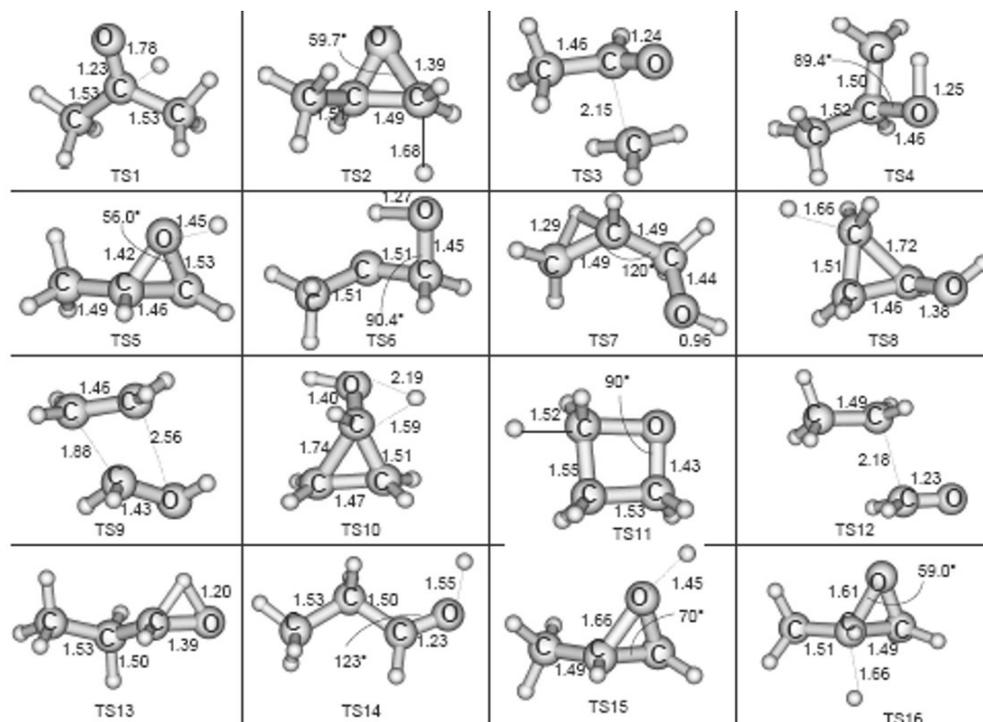
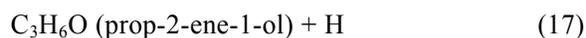


Figure 4. Optimized geometries of transition states for the reaction of $O(^3P_2)$ atom with propyl radicals at the CBS–QB3 level of theory. Distances are in Å.



The optimized geometries of the reactants, products, intermediates and transition states involved in the different pathways for the above mentioned systems are shown in figures 1–4. Schematic diagrams for the different pathways obtained on the lowest doublet potential energy surface using CBS–QB3 model are shown in figures 5–7. Potential energy surfaces obtained from DFT/B3LYP/6-311G(*d, p*) and CBS–Q methods show similar trends and hence are not shown here. The discussion in the next section is based on the results obtained using CBS–QB3 model. CBS–Q energy values are close to CBS–QB3 values in most of the cases. The ZPE-corrected energies are listed in tables 1–3.

3.1 $O(^3P_2) + CH_3$

The attack of $O(^3P_2)$ atom on the carbon atom of the methyl radical produces an intermediate CH_3O (INT1)

and the formation process is estimated to be highly exothermic by -84.78 kcal/mol with respect to the reactant radicals $O(^3P_2) + CH_3$. Two different channels which lead to the products $CH_2 + OH$ and $CH + H_2O$ are not involved in the formation of any intermediate. The former channel is endothermic (13.02 kcal/mol) and latter is exothermic by -12.31 kcal/mol. The intermediate INT1 dissociates and produces $CO + H_2 + H$ with the energy 3.24 kcal/mol higher than INT1. The overall reaction enthalpy is estimated to be -81.54 kcal/mol. There exists another pathway which leads to the formation of $HCHO + H$ via the transition state TS2, INT2 and TS1. As the reaction proceeds along the reaction coordinate, one of the hydrogen atoms migrates from the carbon atom of the methyl radical to the oxygen atom. In TS2, one of the C–H bonds is elongated from 1.11 Å to 1.27 Å. The barrier height for going from INT1 to INT2 is found to be 26.89 kcal/mol. The optimized structure of TS1 is found to be close to that of HCHO suggesting a product like late barrier. The formation of $CO + H_2 + H$ from INT1 is predicted to be the major reaction pathway which is in agreement with the experiment results.⁵ An overview of the potential energy profile for the $O(^3P_2) + CH_3$ reaction is given in figure 5.

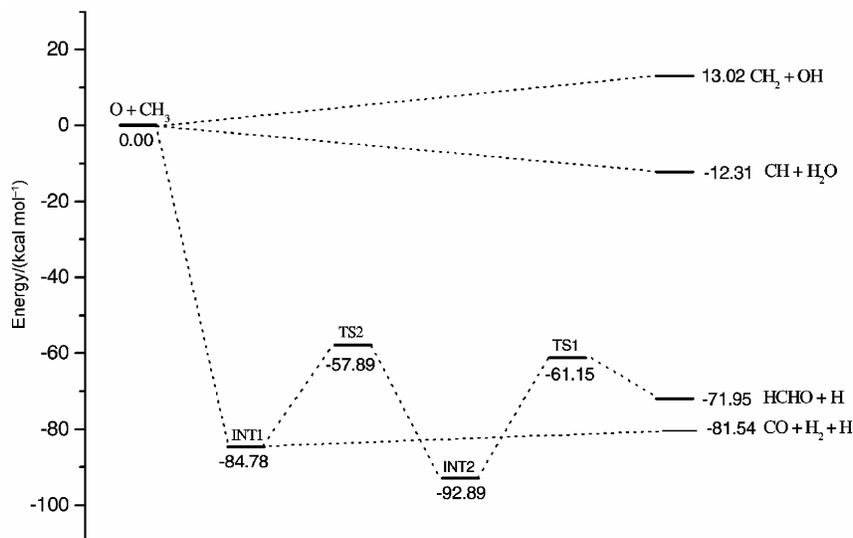


Figure 5. Potential energy profile for the reaction $O(^3P_2) + CH_3$ radical at the CBS-QB3 level of theory.

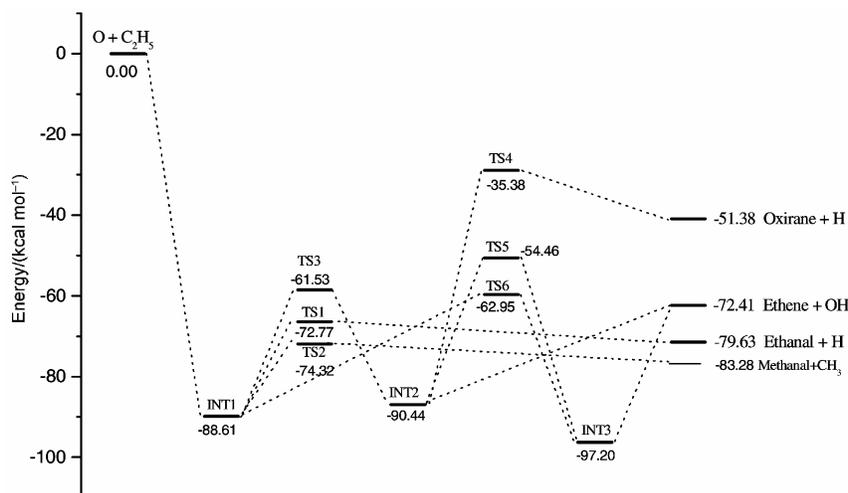


Figure 6. Potential energy profile for the reaction $O(^3P_2) + C_2H_5$ radical at the CBS-QB3 level of theory.

3.2 $O(^3P_2) + C_2H_5$

The attack of $O(^3P_2)$ on C_2H_5 radical results in the formation of a highly exothermic intermediate (INT1, -88.61 kcal/mol). The most facile pathway is predicted to be the formation of methanal + CH_3 ($\Delta H = -83.28$ kcal/mol) via TS2 after taking into account the barrier height, reaction enthalpy, and the number of intermediates involved. The C-C bond is elongated from 1.53 \AA to 2.21 \AA as the reaction proceeds from INT1 to TS2 and finally bond cleavage results in the products. The barrier height is found to

be 14.29 kcal/mol. Another competing reaction channel is the formation of $CH_3CHO + H$, which is actually the abstraction of an H atom from the carbon atom by the oxygen atom through the transition state TS1 (-72.77 kcal/mol). The barrier height in this case is estimated to be 15.84 kcal/mol, which is slightly higher than that for the previous case. Transition state TS4 is a strained cyclic ring. Therefore, it is understandable that there is a barrier of 55.06 kcal/mol in going from INT2 to TS4 and one can conclude that the possibility of the formation of oxirane + H is remote. The formation of the products ethene + OH

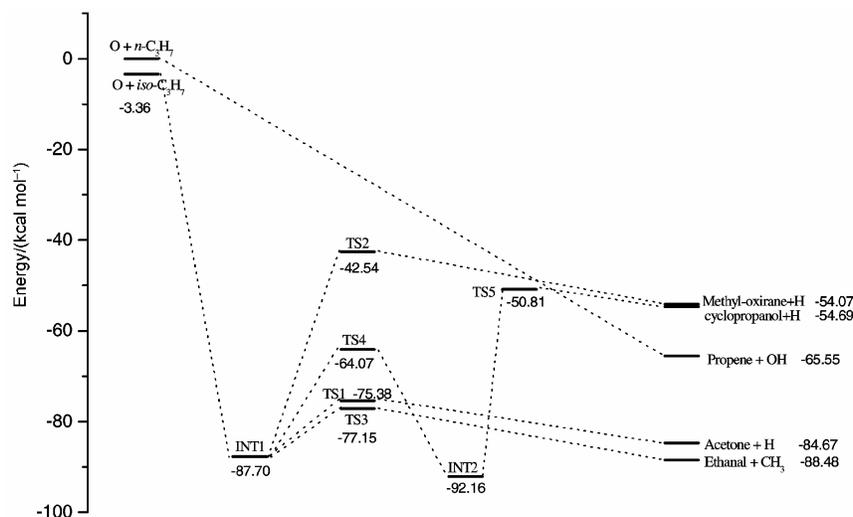


Figure 7. Potential energy profile for the reaction $O(^3P_2) + n\text{-C}_3\text{H}_7$ and *iso*- C_3H_7 radicals through INT1 at the CBS-QB3 level of theory.

Table 1. ZPE corrected energies (kcal/mol) for the various species relative to $O(^3P_2) + \text{CH}_3$ at various levels of theory.

Species	B3LYP/6-311G**	CBS-Q	CBS-QB3
$O(^3P_2) + \text{CH}_3$	0	0	0
$\text{CH}_2 + \text{OH}$	22.35	14.50	13.02
$\text{CH} + \text{H}_2\text{O}$	-1.36	-10.71	-12.31
$\text{HCHO} + \text{H}$	-64.28	-70.32	-71.95
$\text{CO} + \text{H}_2 + \text{H}$	-64.81	-81.43	-81.54
INT1	-88.08	-81.98	-84.78
INT2	-93.36	-91.02	-92.89
TS1	-58.16	-59.61	-61.15
TS2	-55.90	-59.61	-57.89

Table 2. ZPE corrected energies (kcal/mol) for the various species relative to $O(^3P_2) + \text{C}_2\text{H}_5$ at various levels of theory.

Species	B3LYP/6-311G**	CBS-Q	CBS-QB3
$O(^3P_2) + \text{C}_2\text{H}_5$	0	0	0
Oxirane + H	-40.90	-50.41	-51.38
Ethene + OH	-62.27	-66.75	-72.41
Ethanal + H	-71.39	-79.30	-79.63
Methanal + CH_3	-77.81	-83.83	-83.28
INT1	-89.84	-86.77	-88.61
INT2	-89.96	-89.41	-90.44
INT3	-96.25	-96.36	-97.20
TS1	-66.38	-72.60	-72.77
TS2	-71.95	-73.82	-74.32
TS3	-58.43	-61.56	-61.53
TS4	-28.94	-22.44*	-35.38
TS5	-50.51	-54.49	-54.46
TS6	-59.65	-62.60	-62.95

*TS4 was calculated at the second-order Møller-Plesset (MP2) level using the 6-31G(d) basis set

through the intermediates INT1, INT2 and transition state TS3, TS5 is also kinetically and thermodynamically unfavourable. An overview of the different reaction pathways for the $O(^3P_2) + \text{C}_2\text{H}_5$ reaction is given in figure 6.

3.3 $O(^3P_2) + \text{C}_3\text{H}_7$

iso-Propyl radical is estimated to be 3.36 kcal/mol more stable than the *n*-propyl radical. Therefore, it is possible that the conversion of *n*-propyl radical to secondary *iso*-propyl radical will take place readily. Potential energy profiles for the different pathways of the reaction between oxygen triplet atom and propyl radicals are given in figures 7 and 8. The attack of oxygen atom along the central carbon atom of *iso*-propyl radical produces an intermediate (INT1) (highly exothermic, -87.70 kcal/mol), whereas the attack of oxygen atom on *n*-propyl radical would produce INT5 predominantly. As anticipated, the association reaction between the two reactive radical species takes place along INT1 and INT5. Since these addition intermediates possess plenty of internal energy because of the deep potential wells relative to the reactants, it is expected that these intermediates would not re-dissociate into the radical reactants, but undergo subsequent isomerization or decomposition leading to a variety of products. The respective addition reaction mechanisms for the pathways (9)–(19) through the energy-rich intermediates INT1 and INT5 as discussed below.

3.4 Reaction pathways of INT1

Based on the barrier height, reaction enthalpy, and the number of intermediates involved along the reaction coordinates, the most facile pathway is predicted to be reaction (12), which involves the formation of ethanal and methyl radical. This involves C–C bond cleavage via TS3. One of the C–C bonds is elongated from 1.53 Å to 2.15 Å in going from INT1 to TS3. The barrier height for the bond fission is computed to be 10.55 kcal/mol. It lies well within the available energy of the system, and the overall process is calculated to be highly exothermic (–88.48 kcal/mol). The other competing pathway is reaction (10)

Table 3. ZPE corrected energies (kcal/mol) for the various species relative to $O(^3P_2) + n\text{-C}_3\text{H}_7$ at various level of theory.

Species	B3LYP/ 6-311G**	CBS-Q	CBS-QB3
$O(^3P) + n\text{-C}_3\text{H}_7$	0	0	0
$O(^3P) + iso\text{-C}_3\text{H}_7$	–4.15	–2.82	–3.36
Oxetane + H	–39.27	–49.09	–49.10
Methyl-oxirane + H	–42.67	–53.92	–54.07
Cyclopropanol + H	–43.46	–54.61	–54.69
Prop-2-ene-1-ol + H	–49.09	–60.56	–60.69
Cyclopropane + OH	–52.13	–57.48	–57.26
Propene + OH	–61.31	–65.78	–65.55
Propanal + H	–67.01	–76.40	–75.90
Ethene + CH ₂ OH	–68.72	–72.27	–72.33
Acetone + H	–75.27	–85.40	–84.67
Methanal + C ₂ H ₅	–76.87	–80.76	–80.80
Ethanal + CH ₃	–83.98	–89.75	–88.48
INT1	–88.40	–86.84	–87.70
INT2	–87.90	–92.08	–92.16
INT3	–87.34	–89.59	–90.49
INT4	–84.42	–88.44	–88.62
INT5	–86.10	–84.44	–85.94
INT6	–92.22	–94.05	–94.05
TS1	–67.96	–76.47	–75.38
TS2	–33.43	–45.08	–42.54
TS3	–74.08	–77.64	–77.15
TS4	–59.78	–64.06	–64.07
TS5	–40.53	–51.69	–50.81
TS6	–57.67	–61.97	–61.23
TS7	–46.53	–52.22	–52.05
TS8	–31.29	–40.32	–38.30
TS9	–26.04	–33.25	–30.09
TS10	–23.40	–35.28	–31.43
TS11	–19.92	–29.94	–27.00
TS12	–60.85	–73.86	–73.66
TS13	–55.73	–60.25	–59.95
TS14	–60.85	–66.67	–65.20
TS15	–40.53	–51.68	–38.02
TS16	–29.50	–41.13	–38.24

which leads to the product acetone and H atom radical with an overall reaction exothermicity of –84.67 kcal/mol. The transition state TS1 falls in between the INT1 and product acetone + H with a barrier height of 12.32 kcal/mol. In TS1 one of the C–H bonds is elongated from 1.09 Å to 1.78 Å, showing a product like (late) barrier.

Another reaction channel (11) involves the formation of a three-membered cyclic methyloxirane and H atom through TS2 with an overall reaction exothermicity of –54.07 kcal/mol. This channel may not be feasible because of the large barrier involved (45.16 kcal/mol). The geometry of TS2 contains a three membered cyclic ring with one of the C–H bonds elongated. Another channel (8) with nearly the same reaction exothermicity (–54.69 kcal/mol) is the formation of cyclopropanol and H atom through the path INT1–TS4–INT2–TS5. The barrier height between INT1 and TS4 is 23.63 kcal/mol and barrier height between INT2 and TS5 is 41.35 kcal/mol. As the reaction proceeds along the reaction coordinate from INT1, one of the hydrogen atoms is transferred from the C atom to the O atom and forms TS4. A three-membered cyclic ring is formed in TS5 with an elongated O–H bond. Considering the number of intermediates involved and a large barrier height, this reaction is also not likely.

3.5 Reaction Pathways of INT5

For the reaction between $n\text{-C}_3\text{H}_7$ and $O(^3P_2)$, formation of methanal + C₂H₅ seems to be the most favoured channel (16). The reaction proceeds through INT5 (–85.94 kcal/mol) and TS12 (–73.66 kcal/mol). The barrier height is estimated to be 12.28 kcal/mol and the exothermicity of the overall reaction is found to be –80.80 kcal/mol. The attack of oxygen atom on the terminal carbon leads to the formation of INT5 and subsequent cleavage of the C–C bond leads to the products. In TS12 one of the C–C bonds is elongated from 1.53 Å to 2.18 Å.

Another reaction channel (19) results in ethene and CH₂OH. It proceeds through TS6–INT3–TS7–INT4–TS9. The barrier heights are calculated to be between 24.71 kcal/mol for INT5 to TS6, 38.44 kcal/mol for INT3 to TS7 and 58.53 kcal/mol for INT4 to TS9, respectively. The overall reaction exothermicity is found to be –72.33 kcal/mol. The reaction is unlikely to proceed because of the number of intermediates and large barrier heights involved. Another reaction pathway (18) originates in INT5 and pro-

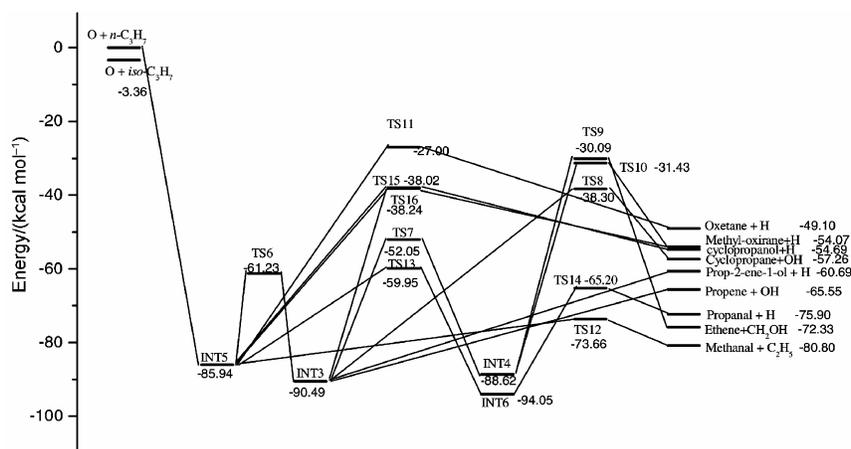


Figure 8. Potential energy profile for the reaction $O(^3P_2) + n-C_3H_7$ and *iso*- C_3H_7 radicals through INT5 at the CBS-QB3 level of theory.

ceeds via TS13, INT6 and TS14 to the products propanal and H atom. The barrier height is calculated to be 25.99 kcal/mol, between INT5 and TS13 and 28.85 kcal/mol, between INT6 and TS14, respectively, with an overall reaction exothermicity of -75.90 kcal/mol. The structure of TS13 shows the transfer of one of the hydrogen atoms from carbon atom attached to the oxygen atom to the oxygen atom whereas in the INT6 complete transfer takes place. The geometry of TS14 shows (elongated O-H bond) product like (late) barrier and the cleavage of O-H bond results in the products.

Another possible reaction channel (14, INT5-TS6-INT3-TS7-INT4-TS10) leads to the products cyclopropanol and H atom. The barrier height is computed to be 24.71 kcal/mol, between INT5 and TS6, 38.44 kcal/mol, between INT3 and TS7 and 57.19 kcal/mol between INT4 and TS10, respectively. As the reaction proceeds from INT5 to INT3, one of the hydrogen atoms is transferred from the central carbon atom to the oxygen atom through TS6. In going from INT3 to INT4, one of the hydrogen atoms is transferred from the terminal carbon atom to the central carbon atom through TS7. Finally the three membered cyclic geometry of TS10 leads to the products cyclopropanol and H atom with an overall reaction exothermicity of -54.69 kcal/mol. This reaction channel does not seem to be feasible because of the number of intermediates and large reaction barriers involved.

Another possible reaction channel (19, INT5-TS6-INT3-TS7-INT4-TS9) leads to the products ethene and CH_2OH with an overall reaction exo-

thermicity of -72.33 kcal/mol. This reaction channel has the same path as discussed in previous case up to INT4. The structure of TS9 clearly shows the elongated C-C bond, which further ruptures and results in the products. This reaction is also unlikely to proceed because of the large barriers involved.

Another possible reaction channel (11) is INT5-TS6-INT3-TS16 resulting in the products methyl-oxirane + H atom. This channel follows the same path as the previous one up to INT3. The barrier height between INT3 and TS16 is estimated to be 52.25 kcal/mol and the overall reaction exothermicity is -54.07 kcal/mol. The geometry of TS16 contains a strained three-membered cyclic ring with an elongated C-H bond (1.66 Å). This reaction channel can be also ruled out on the basis of the number of intermediates and large barrier heights involved.

Another possible channel (13) is INT5-TS6-INT3-TS8 resulting in cyclopropane + OH, with a reaction exothermicity of -57.26 kcal/mol. The path of this reaction is the same up to INT3 as of the previous channel (11) discussed. The three membered cyclic ring with an elongated C-H bond in TS8 clearly shows features of a (product like) late barrier. This reaction also does not seem feasible.

The other possible channels (9 and 17) are INT5-TS6-INT3 to produce propene + OH and INT5-TS6-INT3 to produce prop-2-en-1-ol + H atom. The reaction paths involved are the same as the previous one (11) up to INT3. The overall reaction exothermicities are calculated to be -65.55 kcal/mol and -60.69 kcal/mol, respectively.

Another reaction channel (15) proceeds through INT5–TS11 resulting in oxetane + H atom. The barrier height between INT5 and TS11 is 58.94 kcal/mol with an overall reaction exothermicity is -49.10 kcal/mol. Due to large barrier height and low exothermicity of this reaction, the reaction does not seem feasible.

The other two pathways proceed via INT5–TS15 resulting in cyclopropanol + H atom and INT5–TS16 resulting in methyloxirane + H atom. There is a marginal difference in the energies of TS15 and TS16. The barrier height between INT5 and TS15 is estimated to be 47.92 kcal/mol and that between INT5 and TS16 is 47.70 kcal/mol. The overall reaction exothermicity is -54.69 kcal/mol and -54.07 kcal/mol, respectively. These reaction channels are also unlikely because of the large barrier heights involved.

There exists another possible channel, that is, the formation of propene + OH radical from $O + iso-C_3H_7$ without any barrier and intermediate formation ($\Delta E = -65.55$ kcal/mol).

4. Conclusion

Electronic structure calculations have been carried out to obtain the lowest doublet potential energy surface of the reaction of $O(^3P_2)$ with methyl, ethyl, *n*-propyl and *iso*-propyl radicals using the density functional theoretic method and the complete basis set model. The reaction of $O(^3P_2)$ with various hydrocarbon radicals leads to several energy rich intermediates along the barrierless entrance pathways, which undergo subsequent isomerization and decomposition leading to various products. It is found that the barrier heights, reaction enthalpy, and the number of intermediates involved along the reaction coordinates are of extreme significance in understanding the mechanism for the different pathways. On the basis of thermodynamic and kinetic factors it is predicted that the reaction of triplet oxygen atom with methyl radical results predominantly in $CO + H_2 + H$. In the case of the reaction between triplet oxygen atom and ethyl radical, the formation of methanal and CH_3 radical will be favoured. The reaction between singlet oxygen and propyl radical would lead to the product ethanal and CH_3 radical.

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Supplementary Information in the form of vibrational frequencies is available at (www.ias.ac.in/chemsci)

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