

Theoretical study of the complex reaction of O(³P) with *cis*-2-butene

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Abstract The complex triplet potential energy surface for the reaction of the triplet oxygen atom O(³P) with *cis*-2-butene is investigated at the CBS-QB3 level of theory. The different possible isomerization and dissociation pathways, including both O-additions and H-abstractions, are thoroughly studied. Our calculations show that as found for the *trans*-2-butene reaction, in the high-pressure limit, the major product is CH₃CHC(O)H + CH₃ (P1), whereas in the low-pressure limit the most thermodynamically stable product forms CH₃CO + CH₃CH₂ (P4). The experimental negative activation energy reported for the addition step is very well reproduced at the CBS-QB3 level of theory. Various thermodynamic and kinetic values of interest for these reactions are predicted for the first time. A discussion on the negative activation energy for the addition step of the *trans*- and *cis*-2-butene reactions with O(³P) focussing on the addition reactant complexes is presented.

Keywords Combustion chemistry · Atmospheric reactions · Triplet oxygen atoms O(³P) · *Cis*-2-butene · *Trans*-2-butene · Potential energy surface · CBS

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1 Introduction

The reactions of O(³P) with alkenes are of great importance in a variety of areas such as atmospheric chemistry and metabolic activation of hydrocarbon carcinogens [1]. Particularly, they play an important role in our understanding of combustion processes and oxidation mechanisms of hydrocarbons [2–6].

Since the early 1950s, Cvetanovic [7–12] carried out pioneering studies of the reactions of oxygen atoms O(³P) with olefins in the gas phase. A general reaction mechanism was suggested and summarized in three major steps [13]. First, oxygen atoms in their triplet ground electronic state undergo an electrophilic addition onto the C=C bond, forming adducts that are vibrationally excited triplet biradicals, in agreement with the spin-conservation rule. Second, the triplet biradicals either decompose into products (by H- or CH₂-loss) or carry out intersystem crossing (ISC) to singlet biradicals. The first direct evidence for important H production from C₂H₄ + O was provided by Nicovich and Ravishankara [14]. The triplet biradicals might also isomerize by a hydrogen migration, but this process was found to face a large barrier height and cannot, therefore, compete with direct decomposition [15]. Finally, the singlet biradicals produced from the triplet adducts upon ISC may either convert to “hot” epoxides by ring closure or rearrange by internal migration of H atoms or alkyl groups into “hot” carbonyl compounds. These “hot” compounds may then either undergo collisional stabilization under high-pressure reaction conditions [16, 17] or dissociate rapidly to various products under low-pressure conditions such as molecular beam experiments [18]. An alternative, more energetic, reaction channel is the O(³P) hydrogen abstraction to produce hydroxyl radicals and the corresponding hydrocarbon radical [6].

Oguchi et al. [19] investigated the mechanism of the reaction of $O(^3P)$ with three butene isomers (*trans*-2-, iso-, and 1-butene) and measured the yields of the CH_3 and C_2H_5 radical products using photoionization mass spectrometry. For 1-butene, the fractions of CH_3 and C_2H_5 products were only 0.05 ± 0.01 and 0.29 ± 0.05 , respectively. For *trans*-2-butene, the fractions of CH_3 and C_2H_5 products were 0.52 ± 0.10 and 0.29 ± 0.05 , respectively. The total fraction yield of the CH_3 and C_2H_5 products was 0.81. The rest of the channels accounting for other products remain unclear.

Zhao et al. [20] investigated the reaction pathways for the $O(^3P)$ attack on iso-butene using the MP2 and CBS-4M methods. They predicted the major product channels to be $CH_2C(O)CH_3 + CH_3$, *cis/trans*- $CH_3CHCHO + CH_3$, $(CH_3)_2CCO + H_2$, and $CH_3C(CH_2)_2 + OH$, with the $(CH_3)_2CCO + H_2$ channel being the most energetically favourable. Very recently, Zhao et al. [21] studied the reaction pathways of the $O(^3P)$ with 1-butene using the MP2 and G3 levels of theory. Their results indicate that the site selectivity of the addition of $O(^3P)$ to either carbon atom of the double bond of 1-butene is not significant. The calculated heats of reaction at the G3 level for various product channels are in good agreement with the experimental data.

Our group recently performed the theoretical study of the kinetics and the thermodynamics of the different reaction channels for the reaction between $O(^3P)$ and *trans*-2-butene [22]. Several levels of theory were explored: MP2, PMP2//MP2, CCSD(T)//MP2, CBS-4M, and CBS-QB3. Both CBS methods were able to reproduce the experimental negative activation energy for the addition step and showed similar qualitative trends when comparing the different reaction channels considered. However, the best agreement with experiment for both the kinetic and the thermodynamic data available was achieved at the CBS-QB3 level of theory. The results obtained led to predicting $CH_3CHC(O)H + CH_3$ (P1) as the most abundant product, followed by $CH_3CO + CH_3CH_2$ (P4), in agreement with the experimental data [19].

In this paper, we report the theoretical study of the different reaction channels of $O(^3P)$ with *cis*-2-butene at the CBS-QB3 levels of theory. Both the O-addition and the two H-abstraction channels are explored in detail to determine the main products of these reactions. A comparison with the kinetic and thermodynamic results for the reaction between $O(^3P)$ and *trans*-2-butene [22] is performed. As in the case of the reaction of $O(^3P)$ with *trans*-2-butene, the addition reaction with *cis*-2-butene also exhibits an anti-Arrhenius kinetic behaviour because the Arrhenius activation energy is negative (the rate constant decreases as temperature increases). Activation energy values between 0.36 and -1.46 kcal/mol (corresponding to

standard activation enthalpies, ΔH^\ddagger , between -0.83 and -2.61 kcal/mol) have been reported [23–31]. A brief discussion on this issue focusing on the addition reactant complexes of both reactions is presented.

2 Computational details

Calculations were carried out with the Gaussian 03 suite of programs [32]. Given the good agreement obtained with the experimental data for the *trans*-2-butene reaction with $O(^3P)$ at the CBS-QB3 [33, 34] level of theory [22], the same method was used to perform the study on the *cis*-2-butene reaction. As in the case of the *trans*-2-butene reaction, initial calculations were also performed using the Møller–Plesset perturbation theory truncated at the second order [35] in conjunction with the 6-311G(d,p) basis set and at the CBS-4M [33, 36] levels of theory.

3 Results and discussion

The MP2/6-311G(d,p), PMP2/6-11G(d,p)//MP2/6-311G(d,p), and CBS-4M relative enthalpies and Gibbs free energies are reported in Table S1 of the “Electronic Supplementary Material” (ESM) section. The energies, various (MP2) thermal corrections, enthalpies, and Gibbs free energies (in a.u. at 298.15 K) of the important stationary points along the *cis*-2-butene + $O(^3P)$ addition and H-abstraction channels calculated at different levels of theory are reported in Table S2. The discussion that follows will focus on the CBS-QB3 results.

The Cartesian coordinates of the CBS-QB3 optimized geometries of the stationary structures (reactant, intermediates, TSs, products, and addition reactant complexes) considered in the present study are reported in the ESM section. The CBS-QB3 relative enthalpies and Gibbs free energies for the $O(^3P)$ + *cis*-2-butene reaction are reported in Table 1 (relative to the isolated reactants). The corresponding values for the $O(^3P)$ + *trans*-2-butene reaction [22] are also shown in order to facilitate the comparison between these two reactions. The only experimental value available for the *cis*-2-butene reaction (the activation enthalpy for the addition step reported between -0.83 and -2.61 kcal/mol) is well reproduced with the CBS-QB3 method (-2.24 kcal/mol). The other methods tried were unable to produce accurate results for this quantity.

The same reaction channels investigated for the *trans*-2-butene reaction [22] are explored for the *cis*-2-butene reaction: six addition reaction channels and two hydrogen-abstraction channels (see Scheme S1 in the ESM section). A detailed description of the mechanism studied can be found in Ref. [22]. The sections that follow will address the

Table 1 Experimental and CBS-QB3 enthalpy and Gibbs free energy changes (in kcal/mol, relative to the isolated reactants at 298.15 K) of important stationary points along the addition and H-abstractionreactions of O(³P) with *cis*-2-butene (current work) and *trans*-2-butene (previous work, Ref. [22])

	<i>Cis</i> -2-butene + O(³ P)			<i>Trans</i> -2-butene + O(³ P)		
	ΔH	ΔH_{exp}	ΔG	ΔH	ΔH_{exp}^c	ΔG
CH ₃ CHCOH + CH ₃ (P1)	-30.40		-33.32	-29.83	-29.19	-33.08
CH ₃ CHCOCH ₃ + H (P2)	-23.69		-23.36	-23.89	-23.21	-24.81
CH ₃ CHO + CH ₃ CH (P3)	-13.03		-16.33	-11.81		-15.46
CH ₃ CO + CH ₃ CH ₂ (P4)	-32.29		-36.34	-31.08	-30.86	-35.47
CH ₃ CH ₂ CO + CH ₃ (P5)	-31.31		-34.50	-30.10	-29.90	-33.63
CH ₃ COCH ₂ + CH ₃ (P6)	-31.72		-35.15	-30.50	-30.38	-34.28
CH ₃ CHCHCH ₂ + OH (P7) ^a	-16.50		-18.69	-15.94		-17.91
CH ₃ CHCCH ₃ + OH (P8) ^a	5.02		2.69	5.52		2.99
³ IM1	-27.24		-19.33	-27.07		-19.68
³ IM2	-14.81		-11.86	-13.59		-10.99
³ IM3	-32.06		-31.71	-30.84		-30.84
³ IM4	-34.51		-26.24	-33.30		-25.37
	ΔH	ΔH_{exp}^b	ΔG	ΔH	ΔH_{exp}^c	ΔG
³ TS1	-2.24	(-2.61, -0.83)	5.66	-2.32	(-2.66, -1.20)	5.34
³ TS2	-19.55		-12.00	-18.51		-11.17
³ TS3	-15.47		-7.37	-15.30		-7.35
³ TS4	-9.79		-3.11	-9.20		-3.20
³ TS5	-11.55		-6.15	-10.34		-5.28
³ TS6	-23.92		-16.25	-22.70		-15.38
³ TS7	-20.85		-13.26	-19.63		-12.39
³ TS8	-2.21		4.82	-0.99		5.69
³ TS9 ^a	3.20		10.53	3.21		10.21
³ TS10 ^a	5.12		12.06	5.57		12.75

^a Hydrogen-abstraction products (P7 and P8) and TSs (TS9 and TS10); ^b $\Delta H_{\text{exp}}^b = E_{\text{a exp}} - 2\text{RT}$: -0.83 kcal/mol (Ref. [23], $E_{\text{a exp}} = +0.36$ kcal/mol); -1.42 kcal/mol (Ref. [27, 28], $E_{\text{a exp}} = -0.23$ kcal/mol); -1.45 kcal/mol (Ref. [26], $E_{\text{a exp}} = -0.27$ kcal/mol); -1.46 kcal/mol (Ref. [29], $E_{\text{a exp}} = -0.28$ kcal/mol); -1.48 kcal/mol (Ref. [31], $E_{\text{a exp}} = -0.30$ kcal/mol); -1.51 kcal/mol (Refs. [24, 25], $E_{\text{a exp}} = -0.32$ kcal/mol); -2.61 kcal/mol (Ref. [30], $E_{\text{a exp}} = -1.42$ kcal/mol); ^c see references in Table 1 of Ref. [22]

comparison of the reactions of *cis*- and *trans*-2-butene with O(³P) from a thermodynamic and kinetic points of view.

3.1 The O-addition reactions

The addition of O(³P) can occur at either carbon atom of the double bond of *cis*-C₄H₈ with equal proportion, since this alkene is symmetrical. Figure 1 displays the combined Gibbs free energy profile of the adiabatic channels in the triplet state for the addition pathways calculated at the CBS-QB3 level of theory for the O(³P) reactions with *cis*- and *trans*-2-butene, at 298.15 K, relative to the isolated reactants in each case. The structures of the stationary points calculated for the *cis*-2-butene reaction are also shown.

CBS-QB3 calculates *trans*-2-butene to be 0.87 kcal/mol more thermodynamically stable than *cis*-2-butene. The

standard enthalpy of formation of *trans*-2-butene is 1.22 kcal/mol lower than that of *cis*-2-butene, in good agreement with the experimental value (0.74 kcal/mol). The $\Delta_f H_{\text{gas}}^\circ$ reported for *cis*- and *trans*-2-butene is (-7.7 ± 1.3) and (-10.8 ± 1.0) kJ/mol, respectively [37]. Using thermodynamic tables in standard physical chemistry textbooks [38], *trans*-2-butene has a standard enthalpy and a Gibbs free energy of formation that are 1.00 and 0.69 kcal/mol lower than *cis*-2-butene, respectively.

The addition of O(³P) to the C=C double bond occurs via ³TS1 to form the biradical intermediate ³IM1. The standard Gibbs free energy of activation, ΔG^\ddagger , for the addition step is 0.32 kcal/mol higher for *cis*-2-butene (5.66 kcal/mol) than for *trans*-2-butene (5.34 kcal/mol). The *cis*-*trans* difference for ³IM1 is 0.35 kcal/mol. The calculated addition activation energy for the *cis*- and

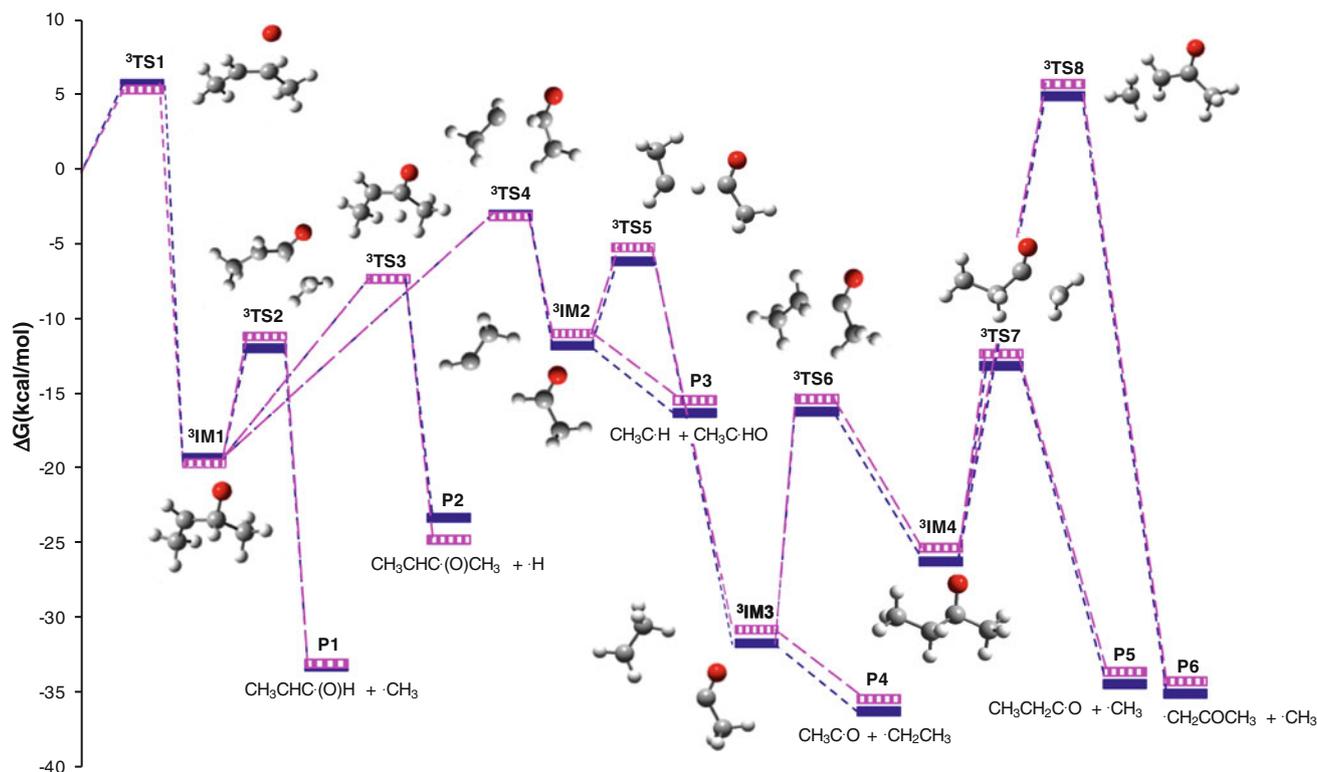


Fig. 1 Combined potential energy profile of the adiabatic channels in the triplet state for the addition pathways of the reaction of *cis*-2-butene (blue solid marker, structures shown) and *trans*-2-butene

(purple marker with vertical pattern) with $O(^3P)$ calculated at the CBS-QB3 level of theory at 298.15 K, relative to the corresponding G values of the isolated reactants in each case

trans-2-butene reactions is -1.06 and -1.14 kcal/mol, respectively, in excellent agreement with the experimental data available (values between 0.36 and -1.46 kcal/mol for *cis*-2-butene [23–31], and values between -0.02 and -1.48 kcal/mol for *trans*-2-butene [39–43]).

Once 3IM1 forms, three fragmentation routes can take place. The least energetic one leads to the most favourable product from a kinetic point of view, P1 ($CH_3CHC(O)H + CH_3$) via 3TS2 . The ΔG^\ddagger for this step relative to 3IM1 is 1.18 kcal/mol lower for *cis*-2-butene (7.33 kcal/mol) than for *trans*-2-butene (8.51 kcal/mol). The second least energetic fragmentation forms P2 ($CH_3CHC(O)CH_3 + H$) via 3TS3 . The ΔG^\ddagger for this step relative to 3IM1 is 0.37 kcal/mol lower for *cis*-2-butene (11.96 kcal/mol) than for *trans*-2-butene (12.33 kcal/mol). The third and most energetic fragmentation leads to P3 ($CH_3C\cdot H + CH_3C\cdot HO$) via 3TS4 . The ΔG^\ddagger for this step relative to 3IM1 is 0.26 kcal/mol lower for *cis*-2-butene (16.22 kcal/mol) than for *trans*-2-butene (16.48 kcal/mol). General observations for this section of the Gibbs free energy profile of the reactions studied are that the higher the ΔG^\ddagger for a given step, the lower the thermodynamic stability of the corresponding products for such a step. The fragmentations from 3IM1 have slightly lower ΔG^\ddagger values for the *cis*-2-butene reactions.

From the reactant complex 3IM2 that leads to P3, a significant section of the reaction profile of Fig. 1 occurs. From a structural point of view, the calculated stationary points of both reactions fully overlap from this point forward. Once the C–C bond of 3IM1 , which was initially a double bond, dissociates via 3TS4 , there are no longer any remains of the initial *cis/trans* isomerization. Hence, the Gibbs free energy difference between the profiles of both reactions is constant from IM2 and equal to 0.87 kcal/mol, the G difference between *cis*- and *trans*-2-butene. This section of Fig. 1 is explained in detail in our previous publication [22]. It is important to note that from 3IM2 , via 3TS5 (with a ΔG^\ddagger of 5.71 kcal/mol), the most thermodynamically stable products, P4 ($CH_3CH_2 + CH_3CO$), form.

The biradical adducts 3IM1 ($CH_3CHC(O)HCH_3$) and 3IM2 ($CH_3CH\cdot CH_3CHO$) lead to the formation of the two most important reaction products P1 and P4. Relative to the isolated reactants in each case, the most favourable products from a kinetic point of view (P1, $CH_3CHC(O)H + CH_3$) are slightly more favoured for the *cis*-2-butene reaction (slightly smaller ΔG^\ddagger by 1.18 kcal/mol). Furthermore, the most thermodynamically stable products (P4, $CH_3CH_2 + CH_3CO$) are also slightly more favoured for the *cis*-2-butene reaction (by 0.87 kcal/mol). The CBS-QB3 calculations show that P1 and P4 are the most

important products for these reactions, in excellent agreement with the experimental findings of Oguchi et al. [19]. The other products are less thermodynamically stable and require larger activation energies in comparison with P4 and P1, respectively.

Overall, the profiles corresponding to the addition of $O(^3P)$ to *cis*- and *trans*-2-butene (see Fig. 1) show qualitative similarities since they follow the same fragmentation routes after the addition adduct is formed and similar stationary points are located. Moreover, from a thermodynamic point of view, the stability order sequence of the products is the same: $P4 > P6 > P5 > P1 > P2 > P3$. The relative Gibbs free energy ordering of the calculated TSs is also the same: $TS1 > TS8 > TS4 > TS5 > TS3 > TS2 > TS7 > TS6$. The main energetic difference between the two reactions is due to the difference in stability between *cis*- and *trans*-2-butene. This stability order also affects the stereochemistry of the TSs and products than conserves some *cis/trans* characters (species before IM2). Looking at relative G values, some stationary points of the *cis*-2-butene reaction are found to be higher in G than those of the *trans*-2-butene reaction (e.g. 3TS1 , 3IM1 , P2), while others are lower in energy (e.g. 3TS2 , 3IM2 , P3). We note that certain stationary points are found to be isoenergetic in two profiles (e.g. 3TS3 , 3TS4).

3.2 The H-abstraction reactions

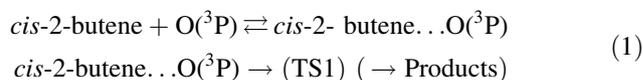
Two possible direct $O(^3P)$ H-abstraction pathways can be considered (see Scheme 1 in the ESM). When the $O(^3P)$ atom attacks the H atom directly attached to the terminal C atom of *cis*-2-butene, the abstraction reaction proceeds via 3TS9 , with a barrier of 10.53 kcal/mol relative to the isolated reactants, leading to the formation of the products P7 ($CH_3CH=CHCH_2 + OH$). This ΔG^\ddagger is 0.32 kcal/mol higher than that of *trans*-2-butene. The $O(^3P)$ atom can also abstract the H atom in the C atom of the double bond; thus, another abstraction reaction occurs via 3TS10 with a barrier of 12.06 kcal/mol (0.69 kcal/mol lower than that of *trans*-2-butene), leading to the formation of the products P8 ($CH_3CHCCH_3 + OH$). Both H-abstraction products are slightly more thermodynamically stable for the *cis*-2-butene reaction.

General characteristics of the H-abstractions to *cis*- and *trans*-2-butene are that the abstraction from the CH_3 group is the most kinetically favoured, as experimentally verified [44], and it leads to more thermodynamically stable products (P7). The addition reaction is much more favoured with barriers of 5.34 and 5.66 kcal/mol. This result is in agreement with experiments [45]; the more substituted the alkene, the smaller the barrier of the addition reaction to the carbon–carbon double bond.

3.3 Negative activation energies and the addition reactant complex

Most reactions (complex or elementary) possess experimental Arrhenius plots that exhibit negative slopes, which indicates that their Arrhenius activation energies are positive quantities and that their rate constants increase with temperature. This is not the case for a significant number of reactions (e.g. OH hydrogen abstractions from some alkenes and aldehydes [46–49]) for which negative activation energies have been reported experimentally. The addition of $O(^3P)$ to very substituted alkenes such as *cis*- and *trans*-2-butene, among others, is also an example of reactions that follow an anti-Arrhenius kinetic behaviour [23–31, 38].

Researchers have come up with a variety of ways to explain this fact [50–53]. One of these explanations, first suggested by Singleton and Cvetanovic when studying the addition step of $O(^3P)$ to alkenes that produces the biradical intermediate [10, 26, 54], focuses on assuming that this reaction is not elementary and that prior to the formation of 3TS1 , a reactant complex forms in a fast reversible step between the initially infinitely separated reactants, as shown in Eq. 1.



The formation of the reactant complex is a barrierless process that is energetically favourable but entropically unfavourable. Its decomposition into the isolated reactants must overcome an energy barrier, but it is an entropically favoured process. Reactant complexes have been experimentally detected in a number of cases, and several theoretical studies focus on their existence [55–64]. Several theoretical studies have considered their formation to properly explain the kinetics of several reactions or negative activation energies [65–70].

Carrying on with the ideas of Singleton and Cvetanovic [10, 26], the addition reactant complexes for the reactions of $O(^3P)$ with *cis*- and *trans*-2-butene were calculated. Their CBS-QB3 structures in the triplet state are shown in Fig. 2. The structural and energetic differences between

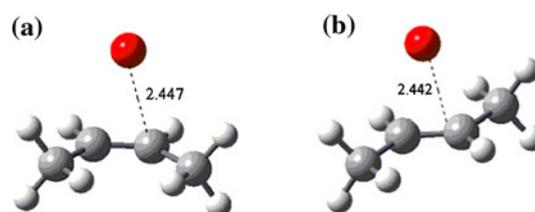


Fig. 2 CBS-QB3 structures of the addition reactant complex for the $O(^3P)$ reaction with **a** *cis*- and **b** *trans*-2-butene

Table 2 Various CBS-QB3 energies (in kcal/mol) for the reactant complex and TS relative to the isolated reactants for the O(³P) addition to *cis*- and *trans*-2-butene

	ΔE (uncorr)	ΔE (0 K)	ΔE (298.15 K)	ΔH (298.15 K)	ΔG (298.15 K)
<i>Cis</i> -2-butene + O(³ P)	0.00	0.00	0.00	0.00	0.00
³ Reactant complex	-2.24	-1.73	-1.29	-1.88	4.52
³ TS1	-1.89	-1.57	-1.64	-2.24	5.66
<i>Trans</i> -2-butene + O(³ P)	0.00	0.00	0.00	0.00	0.00
³ Reactant complex	-2.34	-1.83	-1.38	-1.97	4.33
³ TS1	-1.93	-1.69	-1.73	-2.32	5.34

Energy differences without thermal corrections [ΔE (uncorr)], at 0 K [ΔE (0 K)] and at 298.15 K [ΔE (298.15 K)]; enthalpy [ΔH (298.15 K)] and Gibbs free energy [ΔG (298.15 K)] differences at 298.15 K

these two complexes are almost negligible. The O(³P) atom is symmetrically located at a distance of 2.447 and 2.442 Å from each of the carbon atoms of the double bond in *cis*- and *trans*-2-butene, respectively. This distance (between the oxygen atom and the carbon atom to which it is added) becomes 2.125 and 2.121 Å in ³TS1 of *cis*- and *trans*-2-butene, respectively. The C–O interaction is slightly stronger for *trans*-2-butene than for *cis*-2-butene, and this is also manifested in a slightly lower enthalpy and Gibbs free energy for the complex and ³TS1 relative to the isolated reactants (see Table 2).

Table 2 displays various CBS-QB3 energies for the addition reactant complex and ³TS1 relative to the isolated reactants for each of the two reactions. When the energy differences are calculated using uncorrected energies and at 0 K (using zero-point corrections only), it can be seen that the reactant complex is lower in energy than the TS. Once thermal corrections are added to obtain energies and enthalpies at 298.15 K, both species remain lower in energy than the isolated reactants, but the TS has more negative values than the complex in both reactions. Given that the enthalpy of formation of the TS is lower than the sum of the enthalpies of formation of the isolated reactants, negative enthalpies of activation are calculated (-2.24 and -2.31 kcal/mol for the *cis*- and *trans*-2-butene reactions, respectively), which are in excellent agreement with experiment (see Table 1).

Not all cases of reactions with calculated negative enthalpies of activation (ΔH^\ddagger) lead to negative activation energies (E_a). E_a is the actual experimental quantity to compare with. TST provides a mathematical way to link these two quantities. For bimolecular gas-phase reactions, Eq. 2 is used [71]. For the two cases under study, the experimental activation energy for the addition reaction is negative and the CBS-QB3 results are in excellent agreement. This fact is independent of the existence of a reactant complex.

$$E_a = \Delta H^\ddagger + 2RT \quad (2)$$

When entropic corrections are also accounted for, the calculated relative Gibbs free energies show that both the

reactant complex and the TS are higher in G than the isolated reactants (see Table 2). Hence, for these reactions, the addition reactant complex plays no important role from a kinetic point of view beyond helping to explain the negative activation energies reported as per the idea suggested by Singleton and Cvetanovic [10, 26].

4 Conclusions

In the present work, different reaction channels in the triplet electronic state for the reaction between O(³P) and *cis*-2-butene are examined and compared to the previously calculated mechanism for the *trans*-2-butene reaction at the CBS-QB3 level of theory [22]. The addition of O(³P) to the carbon–carbon double bond is by far the most kinetically favoured reaction. Furthermore, our calculations indicate that similar to what was found when studying the *trans*-2-butene reaction [22], CH₃CHC(O)H + CH₃ (P1) and CH₃CH₂ + CH₃CO (P4) are predicted to be the major products of the reaction for *cis*-2-butene, in excellent agreement with the experimental findings of Oguchi et al. [19].

As in the case of the *trans*-2-butene study [22], the CBS-QB3 method was able to reproduce the experimental value available for the *cis*-2-butene reaction (the negative activation energy for the addition step). Given that most enthalpies of reaction were well reproduced at this level of theory for the *trans*-2-butene reaction as well, this method could be trusted to produce reliable thermodynamic and kinetic data for these reactions.

It has been shown that, following the ideas of Singleton and Cvetanovic [10, 26], the addition reactant complex (which is an energy minimum prior to the addition TS) helps to explain the experimental negative activation energies of the addition of O(³P) to *cis*- and *trans*-2-butene but does not affect the kinetics of these reactions.

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