

## THEORETICAL STUDY OF THE REGIOSELECTIVITY OF THE ADDITION OF THE TRIPLET OXYGEN ATOM TO UNSYMMETRICAL SUBSTITUTED ALKENES

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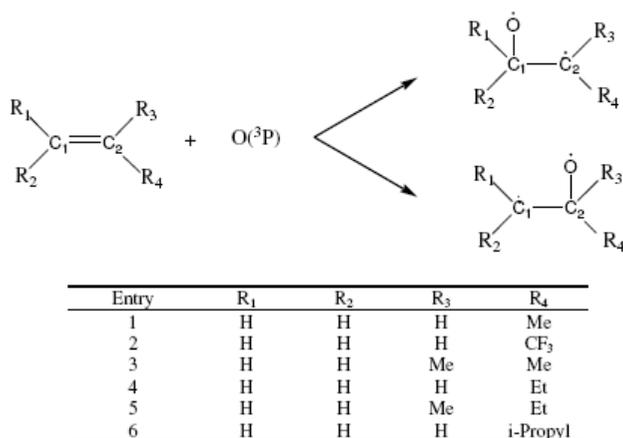
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A theoretical study of the reactivity and regioselectivity of the addition of the triplet oxygen atom  $O(^3P)$  to a series of unsymmetrical substituted alkenes has been performed at the PMP2/6-311++G (d,p) level of theory. Two reaction pathways, namely, the addition to the substituted carbon atom ( $\alpha$ -site) and addition to the non-substituted carbon atom ( $\beta$ -site), have been studied. Our calculations show that the  $\beta$ -addition products are kinetically more favored; whereas the  $\alpha$ -addition products are found to be thermodynamically more stable. The regioselectivity ( $\alpha$  vs.  $\beta$ ) of the addition of the  $O(^3P)$  to the carbon–carbon double bond is predicted by means of the relative energies of the localized transition states and also by the calculation of spin densities of the  $^3\pi\pi^*$  states of reactants and Fukui indices corresponding to the radical attack to alkenes. Our calculations are in good agreement with experimental outcomes.

*Keywords:* Atmospheric reactions; substituted alkenes;  $O(^3P)$  atoms; regioselectivity; *ab initio* calculations.

### 1. Introduction

Unsaturated compounds possessing a carbon–carbon double bond react with various active species in the atmosphere, such as OH and  $NO_3$  radicals,  $O_3$  molecules, Cl, and O atoms.<sup>1–4</sup> More attention has been paid to the reactions of triplet oxygen atom, denoted  $O(^3P)$ , with olefins for their importance in our understanding of combustion processes and oxidation mechanisms of hydrocarbons.<sup>5,6</sup> According to Cvetanovic,<sup>6,7</sup> the  $O(^3P)$  atom, when allowed to react with olefins, first adds to one of the olefinic carbons to give a triplet diradical, which is a key step for the atmospheric degradation of unsaturated compounds (see Scheme 1).



Scheme 1. The two possible channels of the  $O(^3P)$  addition on the carbon–carbon double bond.

Radical addition to alkenes has been extensively investigated since it is a powerful synthetic tool for the formation of intermolecular bonds. A great amount of experimental and theoretical studies devoted to the radical additions to unsymmetrical substituted alkenes can be found in the literature.<sup>8–23</sup> The normal pathway is the radical attack, essentially, at the less substituted carbon atom, namely the  $\beta$  position, although the radical attack at the  $\alpha$  position is also experimentally observed.<sup>24–26</sup>

Using theoretical approaches, Sekusak *et al.* have investigated the reactivity and regioselectivity of the addition of hydroxyl radical to halogenated ethenes and found that the radical attack takes place preferentially on the unsubstituted site.<sup>27</sup> Recently, El-Nahas *et al.* have studied theoretically the relative reactivity and regioselectivity of halogen-substituted ethenes and propene toward the addition of OH radical or  $O(^3P)$  atom, and found that the  $\beta$ -addition products are kinetically more favored whereas the  $\alpha$ -addition products are thermodynamically more favored.<sup>28</sup> Our aim in this work is to perform a theoretical study of the addition of the  $O(^3P)$  atoms to a series of substituted propene and 1-butene compounds (see Scheme 1). The alkene systems under investigation are all unsymmetrical and consequently two reaction pathways can be investigated:

- (i) the  $\alpha$ -addition of the  $O(^3P)$  to the substituted carbon atom of the double bond,
- (ii) the  $\beta$ -addition of the  $O(^3P)$  to the non-substituted carbon atom of the double bond.

The kinetic control of the additions has been put in evidence by calculations of activation energies corresponding to the two reaction pathways while the thermodynamic control of the additions has been predicted by calculations of reaction enthalpies corresponding to the two possible additions. The positional selectivity,

namely  $\alpha$  or  $\beta$ , of addition of the O(<sup>3</sup>P) to the carbon-carbon double bond is predicted by means of the calculation of the difference of activation energies and Mulliken spin densities of the triplet state of the alkene systems and also by the calculation of the Fukui indices corresponding to the radical attack on the  $\alpha$  and the  $\beta$  carbon site of the alkene.

## 2. Computational Details

*Ab initio* calculations were carried out with the Gaussian 03 suite of programs.<sup>29</sup> Using Møller-Plesset perturbation theory truncated at the second-order<sup>30</sup> in conjunction with the 6-311++G(d,p) basis set, we performed full geometry optimizations for the reactants, products, and transition states (TSs) for the addition of O(<sup>3</sup>P) atom to alkene molecules. Restricted (RMP2) and unrestricted (UMP2) methods were used for the closed and open-shell systems, respectively. Spin contamination of the open-shell systems in this study was small. For the doublet radicals and the triplet biradicals, the expectation values of the total spin  $S^2$  were less than 0.76 and 2.01, respectively, after spin annihilations. For the transition states, spin contamination was slightly larger than in the stable radicals; however, all values of  $S^2$  were less than 0.76 and 2.01 after spin annihilations. For each stationary point, we carried out vibrational frequency calculations and examined the vibrational modes by using the GaussView program.

Mulliken spin densities<sup>31</sup> and Fukui indices were calculated in order to predict the regioselectivity of the radical attack. The Fukui function is defined as the first derivative of the electronic density  $\rho(r)$  of a system with respect to the number of electrons  $N$  at a constant external potential  $v(r)$ .<sup>32</sup>

$$f(r) = \left[ \frac{\partial \rho(r)}{\partial N} \right]_{v(r)} = \left[ \frac{\delta \mu}{\delta v(r)} \right]_N. \quad (1)$$

Using left and right derivatives with respect to the number of electrons, electrophilic and nucleophilic Fukui functions for a site  $k$  in a molecule can be defined.<sup>33</sup>

$$f_k^+ = [\rho_k(N+1) - \rho_k(N)], \quad \text{for nucleophilic attack} \quad (2a)$$

$$f_k^- = [\rho_k(N) - \rho_k(N-1)], \quad \text{for electrophilic attack} \quad (2b)$$

$$f_k^0 = [\rho_k(N+1) - \rho_k(N-1)]/2, \quad \text{for radical attack} \quad (2c)$$

where  $\rho_k(N)$ ,  $\rho_k(N-1)$  and  $\rho_k(N+1)$  are the gross electronic populations of the site  $k$  in neutral, cationic, and anionic systems, respectively.

## 3. Results and Discussion

Table 1 summarizes the MP2/6-311++G(d,p) optimized bond lengths of reactants, transition states, and diradical products corresponding to the addition of the O(<sup>3</sup>P) atom to a series of substituted alkenes.

Table 1. Bond lengths (Å) for reactants, transition states, and products.

Entry #	Substrate	Transition state		Product		
		$\alpha$ -Addition	$\beta$ -Addition	$\alpha$ -Addition	$\beta$ -Addition	
1	C1-C2	1.341	1.352	1.350	1.490	1.492
	C2-C3	1.502	1.504	1.495	1.556	1.492
	C-O		1.977	1.970	1.384	1.390
2	C1-C2	1.337	1.347	1.349	1.489	1.493
	C2-C3	1.493	1.506	1.493	1.547	1.487
	C-F	1.349	1.341	1.345	1.337	1.347
	C-O		1.949	1.940	1.388	1.387
3	C1-C2	1.344	1.355	1.351	1.496	1.494
	C2-C3	1.506	1.507	1.500	1.557	1.497
	C2-C4	1.506	1.507	1.500	1.532	1.497
	C-O		1.987	1.970	1.390	1.400
4	C1-C2	1.342	1.353	1.351	1.495	1.494
	C2-C3	1.505	1.508	1.499	1.534	1.497
	C3-C4	1.527	1.527	1.527	1.529	1.536
	C-O		1.977	1.967	1.388	1.389
5	C1-C2	1.345	1.355	1.351	1.552	1.495
	C2-C3	1.508	1.508	1.501	1.496	1.496
	C2-C4	1.509	1.511	1.503	1.537	1.498
	C4-C5	1.535	1.535	1.537	1.530	1.541
	C-O		1.986	1.973	1.399	1.393
6	C1-C2	1.343	1.353	1.351	1.489	1.494
	C2-C3	1.507	1.510	1.501	1.578	1.498
	C3-C4	1.527	1.536	1.527	1.528	1.537
	C3-C5	1.536	1.528	1.537	1.527	1.531
	C-O		1.976	1.963	1.379	1.388

Addition of O( $^3\text{P}$ ) atom to the carbon-carbon double bond leads to a change of the hybridization of carbon atoms of the parent molecules; the  $\text{sp}^2$  carbon atoms become  $\text{sp}^3$ . On going from the parent alkene molecules to the radical products, the bond length between the carbon atoms is increased and, correspondingly, the carbon-carbon bonds are longer for diradical products in comparison with the parent alkene. For instance, O( $^3\text{P}$ ) radical addition to 1-butene substrate lengthens the carbon-carbon bond from 1.342 Å to 1.495 and 1.494 Å in the  $\alpha$ - and  $\beta$ -addition radical products, respectively. We note that the  $\text{C}_1\text{-C}_2$  bonds for  $\alpha$ -products are longer than those of  $\beta$ -products. Inversely, the C-O bonds for  $\alpha$ -products are shorter in comparison with  $\beta$ -products.

Tables 2 and 3 report the total and relative Gibbs free energies of TSs and products corresponding to the two reaction pathways ( $\alpha/\beta$ ) of the addition of the triplet oxygen atom on alkene systems.

Comparison between the  $\alpha$ - and  $\beta$ -additions is quite interesting:

- (i) Both the  $\alpha$  and  $\beta$  additions of the oxygen atom are highly exothermic ( $\Delta\text{H} < 0$ ) and the  $\Delta\text{G}^\circ$  of the reaction ranges from -13.01 to -5.73 kcal/mol.

Table 2. PMP2/6-311++G(d,p) Gibb free energies (in a.u) of reactants and transition states [the Gibbs free energy of the  $O(^3P)$  atom is  $-74.93832$  a.u] and energy differences are in kcal/mol.

Entry #	Reactants	Transition states			
		$\alpha$ -addition	$\Delta G_{\alpha}^{\ddagger}$	$\beta$ -addition	$\Delta G_{\beta}^{\ddagger}$
1	-117.4915302	-192.4086443	13.30	-192.4099393	12.49
2	-414.777237	-489.6893449	16.45	-489.6919649	14.80
3	-156.6670143	-231.5847702	12.90	-231.5870102	11.50
4	-156.6595352	-231.5767519	13.24	-231.5780612	12.42
5	-195.8356599	-270.7537002	12.72	-270.7552471	11.75
6	-195.8318451	-270.7492644	13.11	-270.7501443	12.56

The PMP2 Gibbs free energy values do not indicate a stable pattern when comparing the thermodynamic stability of the  $\alpha$ - and  $\beta$ -addition products. A higher level of theory might need to be used for this.

- (ii) The TSs corresponding to the  $\beta$ -addition are lower in energy in comparison with the  $\alpha$ -TSs. The energy difference ranges from 0.55 kcal/mol (for reaction #6) to 1.64 kcal/mol (for reaction #2). Consequently, the  $\beta$ -additions are found to be kinetically more favored than the  $\alpha$ -additions for all reactions under investigation. In order to confirm the  $\beta$  regioselectivity of the additions of  $O(^3P)$  to substituted alkene systems, we have calculated Mulliken spin densities (MSD) at the  $\alpha$  and  $\beta$  sites of the  $^3\pi\pi^*$  triplet state of alkenes.<sup>27,34–36</sup> The MSD is defined as the difference of the Mulliken charges of spin-up and spin-down electrons. The sum over the Mulliken spin densities equals the total spin of the system. The importance of the relative spin densities in the triplet state in directing the regiochemistry for radical addition could be rationalized considering the state correlation diagram (SCD) model that belongs to the general approach of curve crossing diagrams.<sup>34</sup> The main electronic interactions during radical addition to a double bond can be described as the spin density interactions between the radical and the alkene

Table 3. PMP2/6-311 ++G(d,p) Gibb free energies (in a.u) of reactants and products [the Gibbs free energy of the  $O(^3P)$  atom is  $-74.93832$  a.u] and energy differences are in kcal/mol.

Entry #	Reactants	Products			
		$\alpha$ -addition	$\Delta G_{\alpha}$	$\beta$ -addition	$\Delta G_{\beta}$
1	-117.4915302	-192.449703	-12.46	-192.449738	-12.48
2	-414.777237	-489.724678	-5.73	-489.731709	-10.14
3	-156.6670143	-231.624228	-11.86	-231.623233	-11.23
4	-156.6595352	-231.618591	-13.01	-231.617534	-12.35
5	-195.8356599	-270.793386	-12.18	-270.791524	-11.01
6	-195.8318451	-270.790506	-12.77	-270.790775	-12.94

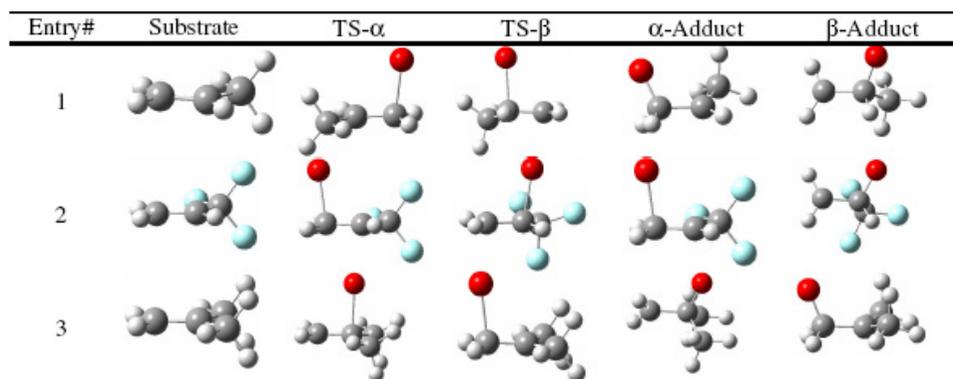


Fig. 1. MP2/6-311++G(d,p) optimized structures of the substrate, transition states and product adducts for the reactions of propene (**1**), 3,3,3-trifluoropropene (**2**) and 2-methylpropene (**3**).

molecules. For the parent alkene molecule, the triplet  $^3\pi\pi^*$  state is described with one unpaired electron on each carbon atom. Substitution in the alkene molecule disturbs the symmetry of the electronic spin density and a carbon atom with higher spin density will be more reactive for radical addition. Figure 1 displays MP2/6-311++G(d,p) optimized structures of the substrate, TSs and product adducts for the reactions of propene **1**, 3,3,3-trifluoropropene **2** and 2-methylpropene **3**.

Figure 2 displays the MP2/6-311++G(p,d) optimized structures of the substrate transition states and product adducts for the reactions of 1-butene **4**, 2-methyl-1-butene **5** and 3-methyl-1-butene **6**.

According to the frontier molecular orbital (FMO) picture, the major orbital interactions in the transition states will occur between the  $\pi$  and  $\pi^*$  orbitals of the

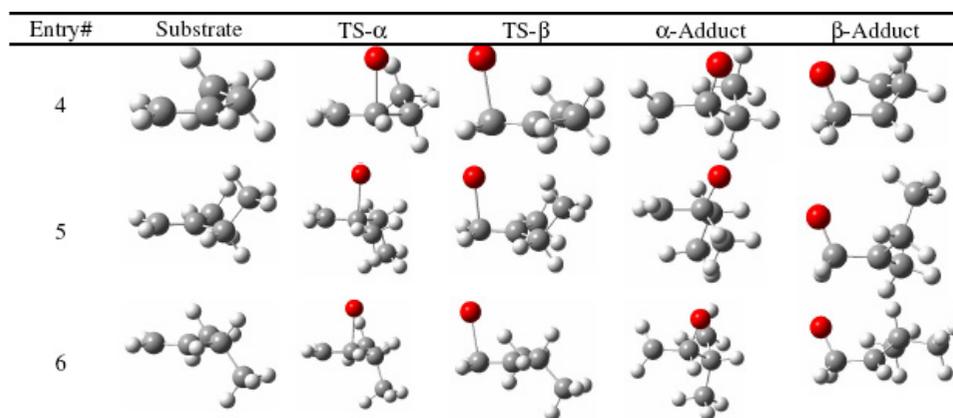


Fig. 2. MP2/6-311++G(d,p) optimized structures of the substrate, transition states and product adducts for the reactions of: 1-butene (**4**), 2-methyl-1-butene (**5**), 3-methyl-1-butene (**6**).

Table 4. Relative spin densities in the state <sup>3</sup>ππ\* and values for the Fukui functions. Highest values are given in bold.

Substrate	<sup>3</sup> ππ* state	Spin density	<i>f</i> <sup>+</sup>		<i>f</i> <sup>-</sup>		<i>f</i> <sup>°</sup>	
			MPA	NPA	MPA	NPA	MPA	NPA
1	C(α)	1.0810	0.1072	0.2351	0.2583	0.3864	0.1828	0.3108
	C(β)	<b>1.2910</b>	0.5921	0.6817	0.2393	0.2773	<b>0.4157</b>	<b>0.4795</b>
2	C(α)	1.1115	0.4078	0.4978	0.1347	0.2232	0.2713	0.3603
	C(β)	<b>1.3235</b>	0.2334	0.3755	0.3496	0.4558	<b>0.2915</b>	<b>0.4156</b>
3	C(α)	0.9659	3.8348	0.0089	0.0775	0.1323	<b>1.9562</b>	0.0706
	C(β)	<b>1.3482</b>	-1.8952	0.0941	0.2122	0.4646	-0.8415	<b>0.2793</b>
4	C(α)	1.0622	-0.0215	-0.0265	0.3734	0.6515	0.1759	0.3125
	C(β)	<b>1.1678</b>	0.8177	0.7988	-0.0035	-0.0684	<b>0.4071</b>	<b>0.3652</b>
5	C(α)	0.9675	-0.3945	-0.0364	0.1690	0.6234	-0.1127	0.2935
	C(β)	<b>1.3347</b>	0.9646	0.8639	0.0481	-0.0846	<b>0.5063</b>	<b>0.3896</b>
6	C(α)	1.2442	0.6644	0.7199	0.3974	0.6624	<b>0.5309</b>	<b>0.6912</b>
	C(β)	<b>1.2724</b>	-0.0167	-0.0503	0.0056	-0.0860	-0.0055	-0.0681

alkene molecule and the SOMO of the O(<sup>3</sup>P) atom. The calculated spin densities corresponding to α and β sites of the <sup>3</sup>ππ\* state of alkenes are given in Table 4.

It turns out that the spin density at the β site is higher than the spin density at the α site for all triplet states of the alkenes, indicating, that the radical attack of the O(<sup>3</sup>P) atom is more favored on the β site.

The regioselectivity of the additions of O(<sup>3</sup>P) atoms to substituted alkene systems could also be rationalized using Fukui indices, *f*<sup>0</sup>, corresponding to the radical attack defined in Eq. (2c). The values of Fukui indices for radical attacks on the α and β sites are reported in Table 4. The atomic gross electron densities were calculated using both Mulliken (MPA) and natural (NPA) population analyses. The tabulated values show that Fukui indices corresponding to the β sites are larger than those corresponding to α sites for all alkene systems except for 3-methyl-1-butene system. In conclusion both calculated spin densities and condensed Fukui functions show that the β regioselectivity is favored over the α regioselectivity. Indeed, according to the pioneering experimental works by Cvetanović<sup>37-39</sup> as well as the recent studies by Washida *et al.*,<sup>40</sup> and Quandt *et al.*,<sup>41</sup> the initial attack of the oxygen atom occurs, preferably, at the lesser substituted position of the double bond, as a consequence of the electron-releasing character of the alkyl groups, which promotes electron density on the non-substituted beta carbon atom.

#### 4. Conclusions

We have carried out *ab initio* calculations on the addition of O(<sup>3</sup>P) to a series of substituted alkenes. The potential energy surfaces corresponding to the two reaction channels α and β were studied at the PMP2/6-311++G(d,p) computational level. Our calculations show that these additions are all exothermic. On the other hand,

the calculated activation barriers show that the  $\beta$ -additions are kinetically more favored than the  $\alpha$ -additions.

The calculated spin densities and Fukui indices show that the attack of the triplet oxygen atom takes place preferentially on the least alkyl-substituted site of the double bond of the alkene system. We note that the regioselectivity for O(<sup>3</sup>P) atom addition to substituted alkenes is not governed by the thermodynamic control (products stability) but by the kinetic control (reaction rates).

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