Theor Chem Acc (2006) 116: 637–640
DOI 10.1007/s00214-006-0109-1

REGULAR ARTICLE

Víctor M. Ramírez-Ramírez · Luis Serrano-Andrés
Ignacio Nebot-Gil

Is the $CH_2OH + O_2 \rightarrow CH_2 = O + HO_2$ reaction barrierless? an ab initio study on the reaction mechanism

Received: 2 September 2004 / Accepted: 28 February 2005 / Published online: 23 February 2006

Abstract The reaction mechanism of the $CH_2OH + O_2$ gas-phase reaction was investigated by means of ab initio calculations. MP2 and QCISD methodologies were used to obtain the stationary points on the potential energy surface. Single-point high-level QCISD(T) calculations were performed over the QCISD results in order to refine the energy of the transition states and the minima found. A new transition state concerning the initial O_2 addition to the CH_2OH radical was found, not reported so far for this reaction. Extra CCSD optimisation and single-point high-level CCSD(T) calculations upon the QCISD results confirm this TS. Additional RASSCF calculations show that its wave function has no significant multireferential character.

1 Introduction

The reaction between α-hydroxyalkyl radicals (RCHOH) and O_2, which commonly occurs in combustion and in atmospheric chemistry [1,2], has long been assumed to be initiated by O_2 addition, followed by HO_2 elimination via a saddle point or transition state (TS) [3–6].

RCHOH radicals, and more precisely the CH_2OH radical, react with O_2 on the last stages of the isoprene and some important monoterpenes degradation pathways [7–9], to form formaldehyde and the hydroperoxy radical.

Previous theoretical calculations by Olivella et al. [10] and Dibble [11] assumed that the initial step is barrierless, by analogy with the CH_3+ O_2 reaction [12]. Also, these previous studies have suggested that the elimination reaction initially starts from a hydrogen bonded adduct:

$$CH_2OH + O_2 \rightarrow HOCH_2OO \qquad (1)$$

$$HOCH_2OO \rightarrow [TS] \rightarrow CH_2 = O—HO_2 \qquad (2)$$

This complex is expected to decompose by simple bond cleavage:

$$CH_2 = O—HO_2 \rightarrow CH_2 = O + HO_2 \qquad (3)$$

However, our results show that there is an initial transition state not predicted so far, for the oxygen addition to the CH_2OH radical. Thus, reaction (1) also goes through a transition state and the corrected reaction scheme would be:

$$CH_2OH + O_2 \rightarrow [TS1] \rightarrow HOCH_2OO \qquad (1')$$

$$HOCH_2OO \rightarrow [TS2] \rightarrow CH_2 = O—HO_2 \qquad (2)$$

$$CH_2 = O—HO_2 \rightarrow CH_2 = O + HO_2 \qquad (3)$$

In this paper, we have studied the detailed mechanism of the $CH_2OH + O_2$ reaction, using some computational methods based on quantum theory.

2 Computational Details

Geometries of all stationary points involved in the CH_2OH+O_2 reaction were optimised at the UMP2/6-31G(d) and QCIS D/6-31G(d) levels of theory. Additional single-point high-level ab initio calculations were also performed at the QCISD(T)/6-31G(d) and QCISD(T)/6-311+G($2df$, $2p$) levels of computation upon QCISD optimised structures. Moreover, some extra calculations were done for the transition state TS1. For this structure, optimisation at the CCSD/6-31G(d) level of theory, and single-point high-level CCSD(T)/6-31G(d) calculations upon QCISD optimised structures were performed. In addition to this, restricted active space SCF (RASSCF) calculations using MOLCAS 5.4 program [13] were done for this precise TS.

The Berny [14] algorithm was employed for the UMP2 and QCISD geometry optimisations. The computed stationary points were characterised as minima or transition states

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Electronic Supplementary Material Supplementary material is available in the online version of this article at http://dx.doi.org/10.1007/s00214-006-0109-1

V.M. Ramírez-Ramírez · L. Serrano-Andrés · I. Nebot-Gil (✉)
Institut de Ciència Molecular, Universitat de València, C/Dr. Moliner, 50, PC: E-46100, Burjassot (Valencia), Spain
Tel.: +34-96-3544333
Fax: +34-96-3543156
E-mail: Ignacio.Nebot@uv.es (I. Nebot-Gil)

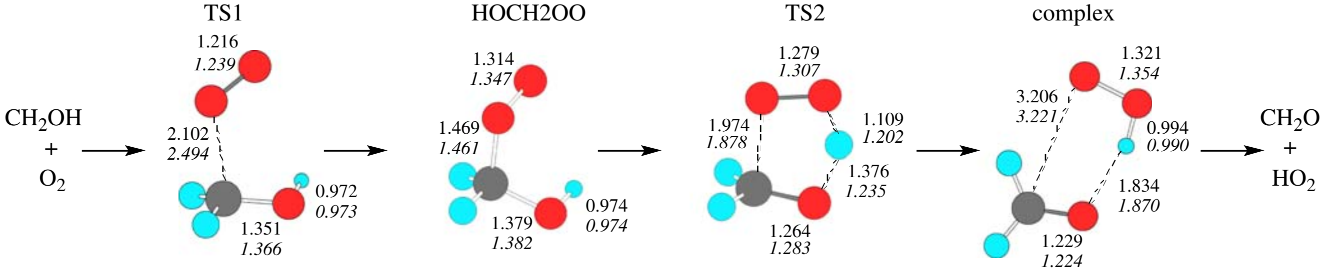

Fig. 1 Optimised structures of all the stationary points along the $CH_2OH + O_2 \rightarrow CH_2O + HO_2$ reaction pathway. The most significant parameters (in Angstroms), at the UMP2/6-31G(*d*) and the QCISD/6-31G(*d*) (in italics) levels of computation are displayed

by diagonalising the Hessian matrix and analysing the vibrational normal modes. According to this, the stationary points were classified as minima if no imaginary frequencies were found, or as transition states if only one imaginary frequency was obtained. The particular nature of a transition state was determined by analysing the motion described by the eigenvector associated with the imaginary frequency. Furthermore, the intrinsic reaction coordinate (IRC) method [15] was used to describe minimum energy paths from transition state structures to the corresponding minima at the UMP2 and QCISD levels of calculation. The eigenfollowing and TS methods [16] were employed for locating the minima and transition state structures.

Zero-point energies (ZPE) were computed at the MP2 and QCISD levels of theory, and to obtain the energies at 298.15 K, the thermal correction of each species was added.

Single reference calculations were performed with the GAUSSIAN 98 [17–19] set of programs on a SGI Origin 2000 and on a SGI Altix 3300 Itanium 2 Processor 1,400 MHZ of the Theoretical Chemistry Group of the University of Valencia (Spain).

3 Results and discussion

The calculations carried out in this Letter have shown the detailed mechanism of the $CH_2OH + O_2$ reaction. After doing a thorough study of the potential energy hyper surface (PEHS), we have found all the stationary points involved in the mechanism and a transition state for reaction ($1'$) not predicted so far.

3.1 Structures of the stationary points found

Figure 1 depicts the geometries of the intermediate $HOCH_2OO$, the hydrogen bonded complex $CH_2 = O—HO_2$, and both transition states (TS1 and TS2) found along the reaction mechanism. None of the molecules involved in the reaction pathway presents any symmetry. The structural parameters for reactants, products and intermediates, at both the UMP2/6-31G(d) and the QCISD/6-31G(d) levels of theory are shown. As seen in this figure, bond distances are similar for both MP2 and QCISD methodologies. The results are in good agreement with the previous theoretical works [10, 11], where CASSCF and B3LYP functionals were used as computational methods.

The most significant difference between MP2 and QCISD results is found in TS1. The distance between oxygen and the carbon atom in the CH_2OH radical is 2.102 Å for MP2 and 2.494 Å for QCISD calculations. This larger bond distance for the QCISD structures results in a quite low imaginary frequency ($166.3i\ cm^{-1}$), opposite to the one found for the MP2 calculations ($675.8i\ cm^{-1}$) (for a detailed description of the harmonic vibrational frequencies of all the stationary points involved in the CH_2OH reaction with O_2, consult the supplementary material, Table 1S).

At CCSD/6-31G(d) level, the TS1 C–O distance is 2.451 Å, very close to the QCISD value. However, at this latter level, the convergence in the geometry optimisation was achieved only with the GAUSSIAN 98 numerical procedure, but the final analytical convergence test failed. This means that in spite of the fact that only an imaginary frequency ($212.5i\ cm^{-1}$) was found (as corresponds to a transition state), the maximum displacement and the RMS displacement items in the GAUSSIAN convergence criteria did not converge.

In TS2 the position of the H atom that is being transferred determines the imaginary frequency of each method ($746.8i\ cm^{-1}$ for MP2 and $1258.6i\ cm^{-1}$ for QCISD level of theory).

3.2 Comments about the reaction mechanism

Bond distances in Fig. 1 illustrate clearly how the reaction takes place. First of all, an oxygen addition to the hydroxymethyl radical occurs. This reaction was considered barrier-free in previous works [10, 11], by analogy with the $CH_3 + O_2$ reaction, as reported by Walch [12]. However, we show here that it proceeds through a saddle point (TS1). This transition state is not related to any van der Waals complex, or at least, we did not find any. Then, the intermediate generated may undergo a further concerted HO_2 elimination through a five membered ring-like transition structure (TS2) with the subsequent formation of the hydrogen bonded complex $CH_2 = O—HO_2$. This complex finally gives the reaction products. Olivella et al. [10] investigated other possibilities such as rearrangement forming an intermediate OCH_2OOH

Table 1 Reaction enthalpy, barrier heights for transition state structures TS1 and TS2, and stabilisation energy for the intermediate $HOCH_2OO$ and the complex $CH_2 = O—HO_2$, with respect to reactants at different levels of calculation

Method[a]	ΔH_r^0	ΔE_{TS1}	ΔE_{TS2}	ΔE_{Int}	$\Delta E_{complex}$
MP2(Full)/6-31G(d)	−50,38	51,59	−58,12	−108,3	−84,52
PMP2(Full)/6-31G(d)	−36,23	−0,42	−47,07	−94,43	−70,67
QCISD/6-31G(d)	−83,26	0,38	−62,80	−139,7	−115,0
QCISD(T)/6-31G(d)//BS1[b]	−83,39	−3,01	−78,03	−140,4	−116,1
QCISD(T)/6-311+G(2df,2p)//BS1	−79,16	−1,17	−86,40	−142,4	−106,8

[a] All relative energies calculated in this table (in kJ mol^{-1}) include ZPE and thermal corrections

[b] BS1 represents the structures optimised at the QCISD/6-31G(d) level of theory

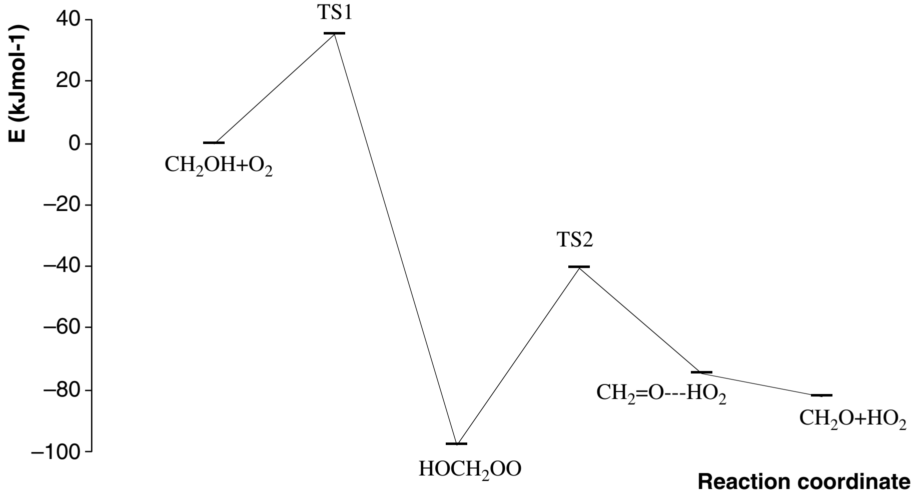

Fig. 2 QCISD(T)/6-311+G($2df$, $2p$)//QCISD/6-31G(d) Gibbs Free Energy profile for the reaction between CH_2OH and O_2. Relative energies with respect to reactants, are given in kJ mol^{-1}

and subsequent decomposition to form the final products, but their results showed that the barriers involved in these reactions are too high and these processes do not compete with the proposed mechanism.

Also, another conformer of the planar complex $CH_2 = O—HO_2$ was found by Dibble [11], but it is higher in energy, and shows an imaginary frequency at MP2 level.

3.3 Energetic considerations

Table 1 displays the numerical data corresponding to reaction enthalpy, barrier heights for the transition states TS1 and TS2, and stabilisation energy for the intermediate $HOCH_2OO$ and the hydrogen bonded complex $CH_2 = O—HO_2$, at different levels of calculation.

The global reaction is exothermic for all the methodologies employed. Figure 2 shows an energy profile for the reaction pathway calculated at QCISD(T)/6-311+G($2df$, $2p$) //QCISD/6-31G(d) level. ΔH_r^0 for the overall reaction is $-79.16\,kJ\,mol^{-1}$. TS1 is found to be very close in energy to reactants, and then, the energy barrier can be positive or negative, depending on the method of calculation. For the QCISD/6-31G(d) optimisations, the calculated energy barrier has a value of $0.38\,kJ\,mol^{-1}$, and for our most accurate level of calculation, a negative barrier of $-1.17\,kJ\,mol^{-1}$ was found. Further work concerning these kinds of transition states corresponding to oxygen addition to radicals must be done in future, in order to determine the precise nature of the TS. Table 1 shows how the intermediate $HOCH_2OO$ formed is strongly stabilised; thus, the next transition state (TS2), in spite of having an energy of $56.02\,kJ\,mol^{-1}$ higher than the intermediate, is easily overcome once the products have passed through TS1, since the kinetic energy is high enough above the $56.02\,kJ\,mol^{-1}$. When the second transition state is passed, the complex $CH_2 = O—HO_2$ is formed, which has less energy than TS2, but is less stabilised than the intermediate ($-106.82\,kJ\ mol^{-1}$) with respect to reactants. This complex gives the final products by bond cleavage without any energetic barrier.

3.4 Adequacy of the theoretical methods employed

All stationary points involved in the oxidation reaction were treated with a single-reference based wavefunction. The T_1 diagnostic value was calculated for each stationary point of the PEHS, to ensure that this treatment is correct. The results are summarised in Table 2, together with the S^2 average values. The T_1 diagnostic gives a qualitative assessment of the significance of nondynamical correlation. Hence, the larger the T_1 value is, the less reliable the results of the

Table 2 T_1 diagnostic values, and spin eigenvalues of the unrestricted wavefunction and its projection for all stationary points of the $CH_2OH + O_2 \rightarrow CH_2 = O + HO_2$ reaction

Species	QCISD/6-311+G(2df,2p)[a]	UHF/6-311+G(2df,2p)	PUHF/6-311+G(2df,2p)
	T_1	$\langle S^2 \rangle$	$\langle S^2 \rangle$ A
CH_2OH	0.0171	0.76	0.75
O_2	0,0181	2.05	2.00
TS1	0.0337	1.73	0.91
$HOCH_2OO$	0.0307	0.76	0.75
TS2	0.0289	0.78	0.75
CH_2=O—HO_2	0.0302	0.76	0.75
CH_2=O	0.0171	0	0
HO_2	0.0346	0.76	0.75

[a] All magnitudes have been calculated upon QCISD/6-31G(d) optimised structures.

single-reference coupled cluster wavefunction are. For closed-shell systems, values over 0.02 are suspect. Formaldehyde is our only closed shell system, and its T_1 value (0.0171) is clearly under the limit. Concerning the cut-off open-shell systems, Lee and Taylor [20] suggest that T_1 values may be larger. In fact, we can find values of 0.045 accepted as reliable in the work of Rienstra-Kiracofe et al. [21], and Peiró et al. [22] also tested the QCISD methodology in these kinds of systems, comparing their results with those obtained with a multi-reference method. Therefore, our highest value of 0.0337 obtained for TS1 should be considered clear of suspicion. Also, at CCSD(T)/6-31G(d)//QCISD/6-31G(d) level, the T_1 diagnostic value for TS1 is 0.0315, suggesting again the monoreferential character of its wavefunction. To confirm this finding, a full-valence RASSCF calculation, involving 19 orbitals and 25 electrons in the active space, was carried out at the MP2 optimised geometry, by means of the MOLCAS program. The result reveals that the wave function can be considered well defined by a single configuration (87%). Moreover, several attempts to optimise the TS1 geometry were made with the RASSCF method including up to triple excitations, with the help of MOLCAS program. Unfortunately, optimisations at this level of theory failed to locate the TS1 structure.

Table 2 also includes $\langle S^2 \rangle$ values calculated at UHF/6-311+G($2df$, $2p$) level. Only TS1 shows a significant amount of spin contamination, less important after proper projection of the wavefunction. At QCISD level of theory there is not spin contamination after annihilation of unwanted spin states.

4 Conclusions

By means of ab initio theoretical methods, the $CH_2OH + O_2$ reaction mechanism has been analysed and the nature of the stationary points involved has been determined. Our results have shown the presence of a transition state structure for the oxygen addition to the CH_2OH molecule step, not considered in previous works. This barrier has an energy value similar to reactants, but could have a decisive influence over the global reaction. Further work on these kinds of transition state structures for O_2 additions to radicals is required. Previous MultiWell calculations [11] have shown that the chemically activated $HOCH_2OO$ radical, that does not promptly fall apart to reactants, is transformed to $CH_2 = O + HO_2$ through TS2. Our results confirm that. Apart from TS1, the rest of stationary points found are in good agreement with previous theoretical works done on this reaction.

Acknowledgements V. M. R. R. thanks the Conselleria d'Educació I Ciència for a personal grant. This work was supported by Spanish DGES (Project BQU2001-2935-002-01) and CCEC (Projects INF00-15 and INF01-051). The authors also thank the OCYT for its financial help to their group (GRUPOS03/173 and INFRA03/047).

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