Quantum chemical study on the atmospheric photooxidation of methyl vinyl ether (MVE)

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ABSTRACT

The reactions of methyl vinyl ether (MVE, $CH_3OCH{=}CH_2$) with OH radicals have been studied using density functional theory (DFT/B3LYP) with the 6-31G* basis set. The geometries and frequencies of all the stationary points and the minimum energy paths (MEPs) are calculated at the B3LYP/6-31G* level. The energetic information along the MEPs is further refined at the MP2/6-311 + G** level of theory. Three reaction pathways have been considered: one H abstraction and two OH additions to >C=C< bonds. A complete description of the possible degradation mechanisms in the presence of O_2 and NO_x has been calculated and discussed. The detailed profiles of the potential energy surfaces (PESs) for the reactions are also explained. The calculations show that the most energetically favorable isomer is that of OH addition to the terminal carbon positions (C3 atom). The main products of the OH-initiated atmospheric photooxidation of MVE are methyl formate, formaldehyde and the glycolic acid methyl ester.

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1. Introduction

Oxygenated volatile organic compounds (OVOCs) are widely used in manufacturing process as solvents in paints, pharmaceutical process synthesis and adhesives [1]. These species are emitted directly into the troposphere by evaporation. Such compounds have some direct or indirect damaging effects on the environment or on human health [2].

Vinyl ethers (CH=CHOR, where R is an alkyl group or Ph) have been used as new solvents to replace traditional ones in order to reduce such damaging health effects. Until now these ethers are used in different industries, particularly as solvents, motor oil additives, and as intermediates for the synthesis of flavors, fragrances and pharmaceuticals [3,4]. Since they are of common use, the emission into the atmosphere may greatly rise. Upon their release into the atmosphere, these compounds will undergo either photolysis or photochemical oxidation by OH radicals and ozone during daytime and by nitrate radicals (NO_3) and ozone during the nighttime. Reactions with Cl atoms may also be important in certain locations during certain times of the year. Among these various reactions, OH radicals play the most essential role in determining the oxidation power of the atmosphere. These chemical processes may play an important role in the chemistry of the polluted troposphere such as the contribution to the formation of ozone and secondary pollutants [5]. Precisely assessing the atmospheric impact appears to be highly desirable for photochemical remediation.

To date, studies on the atmospheric chemistry of vinyl ethers have not been performed to a significant extent. A limited number of studies focus on the structure of methyl vinyl ether (MVE, $CH_3OCH{=}CH_2$) [6–8], the kinetic and product study of the OH [5,9–12] and NO_3 [5,10–13] radicals and O_3 [10–13] -initiated oxidation reactions.

As the simplest vinyl ether, methyl vinyl ether ($CH_3{-}O{-}CH{=}CH_2$, MVE) has been investigated. The experimental kinetic and product studies of the gas-phase reaction of OH radicals with MVE have been found in literature. Thiault and Perry [5,9] have measured the OH-oxidation rate constants in different temperature ranges. Klotz et al. [10] has studied the mechanisms of OH-initiated oxidation of MVE in which the main products (methyl formate and formaldehyde) were provided and the simple degradation mechanisms were proposed to explain their observed products. They also pointed out that other products such as 2-hydroxy-3-oxa-butanal and glycolic acid methyl ester should exhibit, but the reference spectrum of 2-hydroxy-3-oxa-butanal is not currently available. In addition, they did not confirm whether vinyl formate produced through H abstraction exhibits or not and guessed that vinyl formate will react rapidly with OH to form formic anhydride. All these assumptions needed to be validated but they could not be reached experimentally under considered conditions. Theoretical computations can provide accurate potential energy surfaces (PES) which can assist to explain experimental observations and can give the structures of radical intermediates

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and transition states. This information is not only suitable for judging whether a reaction pathway is favorable or not, but also can provide new findings that could not be reached experimentally. Therefore, as a supplement to this experimental study and to assess the potential environmental impacts of vinyl ethers, we present the theoretical study on the OH-initiated atmospheric photooxidation reaction of MVE. In this paper the potential energy surface and energetically favorable pathways are provided.

2. Computational details

All the calculations reported were performed with GAUSSIAN03 suite of programs [14]. Methyl vinyl ether (MVE, $CH_3OCH=CH_2$) is selected as the reactant. The geometries of reactants, products and transition states were fully optimized by using density functional theory (DFT) with Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP) [15,16] with the 6-31G* basis set. This has been used successfully in previous study for related compounds [8]. The corresponding harmonic vibrational frequency calculations at the same level are used to characterize all stationary points as either minima (no imaginary frequencies) or transition states (one imaginary frequency). To verify that transition states actually connect to the expected reactants, intermediates and products for each reaction, intrinsic reaction coordinate (IRC) [17] calculations were performed. Single-point energy calculations with the MP2/6-311 + G** basis set are made on the basis of 6-31G(d,p)-optimized geometry and denoted it as MP2/6-311 + G**//B3LYP/6-31G*. The energies emerging in this paper include the ZPVE corrections unless otherwise specified.

3. Results and discussion

The optimized structures of the transition states for the reaction of MVE with OH radicals are depicted in Fig. 1. Figs. 2 and 3 show the optimized transition state structures of the reaction of IM1, IM2 and IM4 with O_2/NO. The geometrical structures of all stationary points along the potential energy surface (PES) are shown in Supporting information (Figs. S1, S2 and S3). Figs. 4 and 5 show the energy profiles for the OH addition reaction in the presence

of O_2/NO, respectively. The energy profiles of H abstraction reaction in the presence of O_2/NO are shown in Fig. 6.

3.1. The reaction of MVE with OH radicals

There is one >C=C< double bond in the structure of MVE and therefore the OH addition to the carbon–carbon double bond is a possible reaction pathway for the reaction of MVE with OH radicals. Since the two carbon atoms in —CH=CH$_2$ are unequivalent, two OH addition reaction pathways are considered. In addition, OH is one strongly nucleophilic radical, H abstraction from MVE should be another possible reaction channel. According to the properties of H atoms in MVE, three H abstraction reaction processes are considered in this paper. Thus, five possible reaction pathways, R1—R5, were identified for the reaction of MVE with OH radicals. The reaction scheme is as follows:

MVE + OH → TS1 → IM1	R1	Association–elimination
→TS2 → IM2	R2	Association–elimination
→IM3 → TS5 → IM4 + H_2O	R3	H abstraction
→IM3′ → TS5′ → IM4′ + H_2O	R4	H abstraction
→IM3″ → TS5″ → IM4″ + H_2O	R5	H abstraction

3.1.1. Association–elimination pathways

In the OH addition pathway two sites (C2 and C3 sites) are available for the addition of the OH radical because there are two unequal carbon atoms in carbon–carbon double bond. Therefore, two reaction pathways, R1 and R2, are found and reported in this work. The van der Waals complexes have not been searched for, since they are difficult to be found at the DFT level, and moreover, they are not chemically relevant in the reaction mechanisms [18] proposed (while they may exist). The first step in the reaction mechanism is the formation of two radical adducts (OH—MVE IM1 and IM2) through the transition states TS1 and TS2. The relative energies of TS1 and TS2 are 7.88 and 4.40 kcal/mol. In the structures of IM1 and IM2 the bond lengths of O2—C2 and
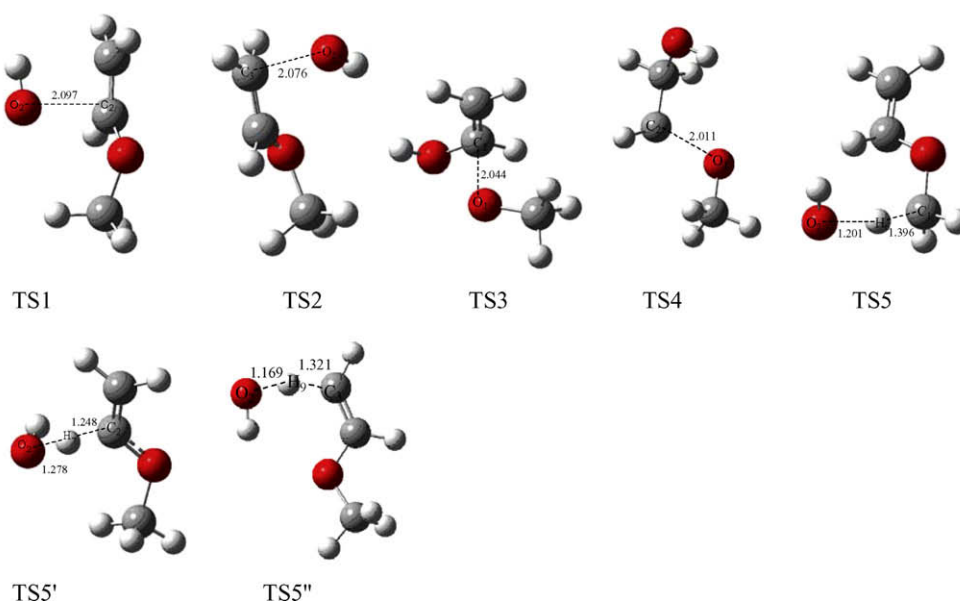

Fig. 1. B3LYP/6-31G* optimized transition state structures for the reaction of MVE with OH radicals in which bond lengths are in Å.
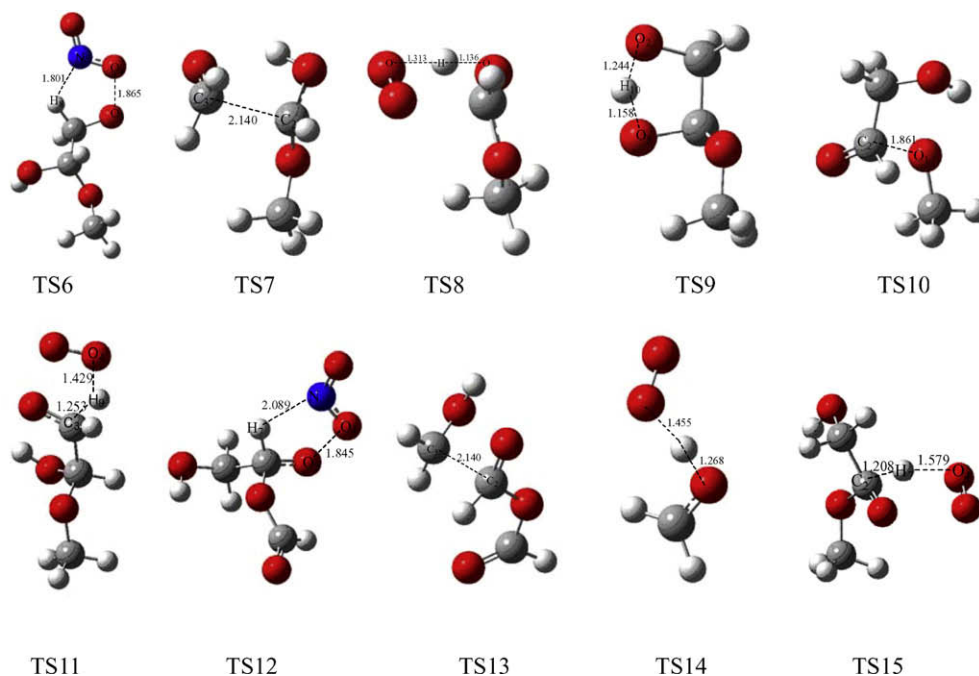
Fig. 2. B3LYP/6-31G* optimized transition state structures for the secondary reactions of IM1 and IM2 with O_2/NO in which bond lengths are in Å.
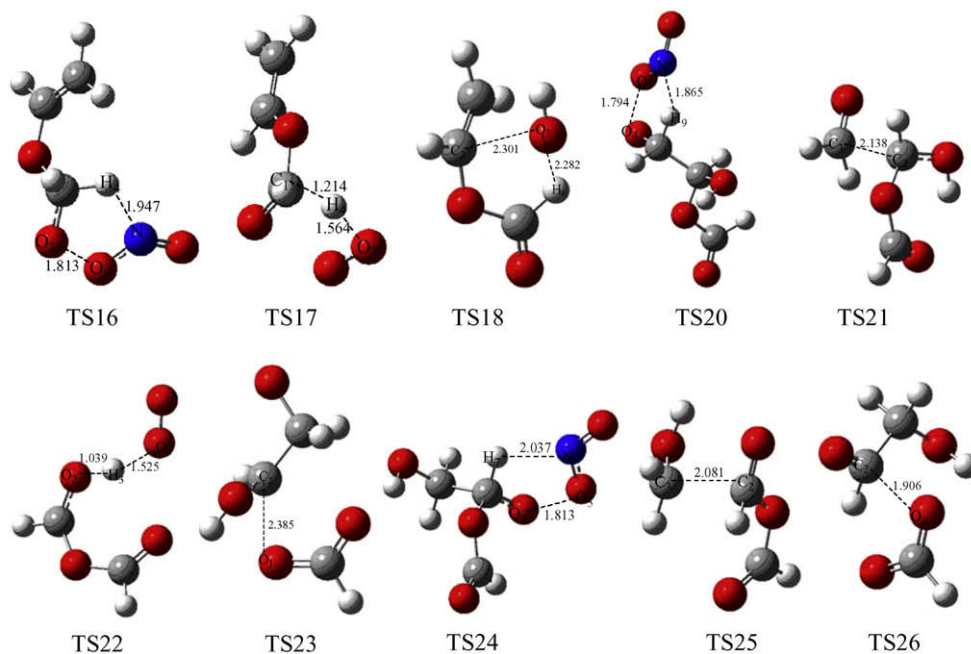

Fig. 3. B3LYP/6-31G* optimized transition state structures for the secondary reactions of IM4 with O_2/NO in which bond lengths are in Å.

O2—C3 are 1.425 and 1.441 Å, respectively. The energies of IM1 and IM2 are 43.85 and 38.00 kcal/mol lower than the total energy of the separate reactants (MVE and OH), respectively. The IM1 and IM2 are energy-rich adducts which can react via unimolecular decomposition and/or with atmospheric O_2/NO.

The decompositions of IM1 and IM2 result in the formation of the following products: CH_3O, CH_2CHOH and $CHCH_2OH$. The processes involve the cleavage of the C2—O1 bond through the transition states, TS3 and TS4, respectively. In TS3 the bond length of C2—O1 is 2.045 Å which is longer about 0.556 Å than that in IM1. In TS4 structure, the length of C2—O1 bond is 0.643 Å longer than the equilibrium value of 1.368 Å in IM2. The decomposition pro-

cesses have higher potential energy barriers of about 40.85 and 43.22 kcal/mol, respectively, indicating that the decompositions of IM1 and IM2 are energetically unfavorable and will not take place. The products $CH_3O\cdot$, $CH_2CHOH\cdot$ and $CHCH_2OH\cdot$ will be impossible products for the reaction of MVE with OH radicals. Therefore, IM1 and IM2 will mainly react with O_2/NO as their removal pathway in the troposphere.

3.1.2. H abstraction channels

Three kinds of hydrogen atoms are found in MVE: one in the CH_3O group and the other two attached to the carbon–carbon double bond. Thus, three pathways, R3, R4, and R5, were considered: H

Fig. 4. The energy profiles for OH-initiated atmospheric photooxidation of MVE according to pathway R1 in which the energy values are in kcal/mol and are relative to reactants.

Fig. 5. The energy profiles for OH-initiated atmospheric photooxidation of MVE according to pathway R2 in which the energy values are in kcal/mol and are relative to reactants.
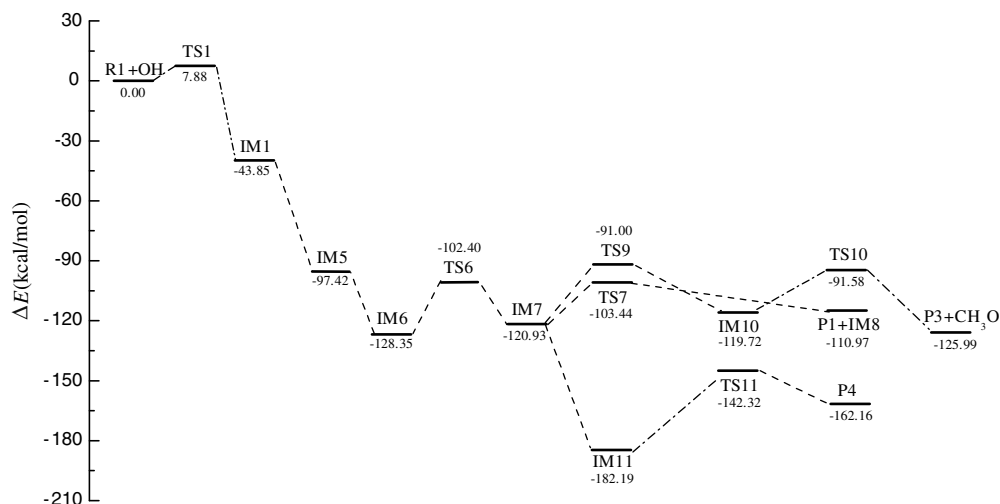

Fig. 6. The energy profiles for OH-initiated atmospheric photooxidation of MVE according to pathway R3 in which the energy values are in kcal/mol and are relative to reactants.
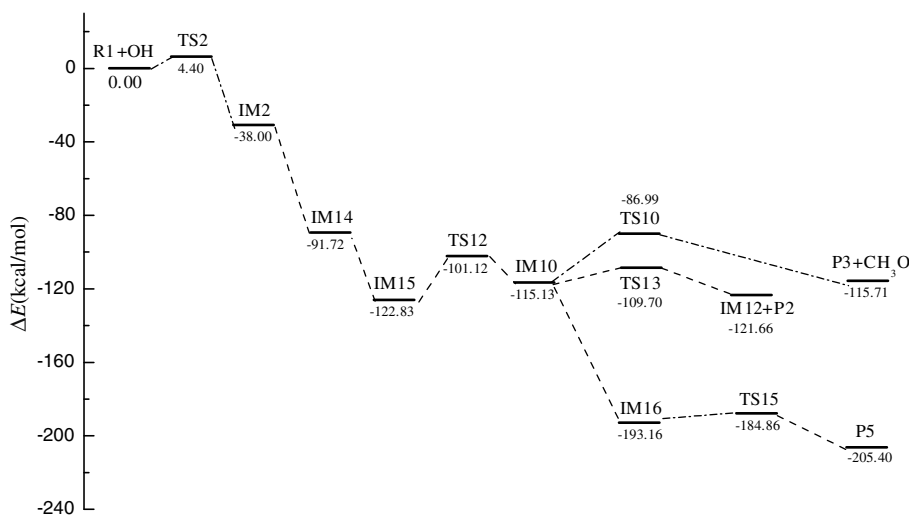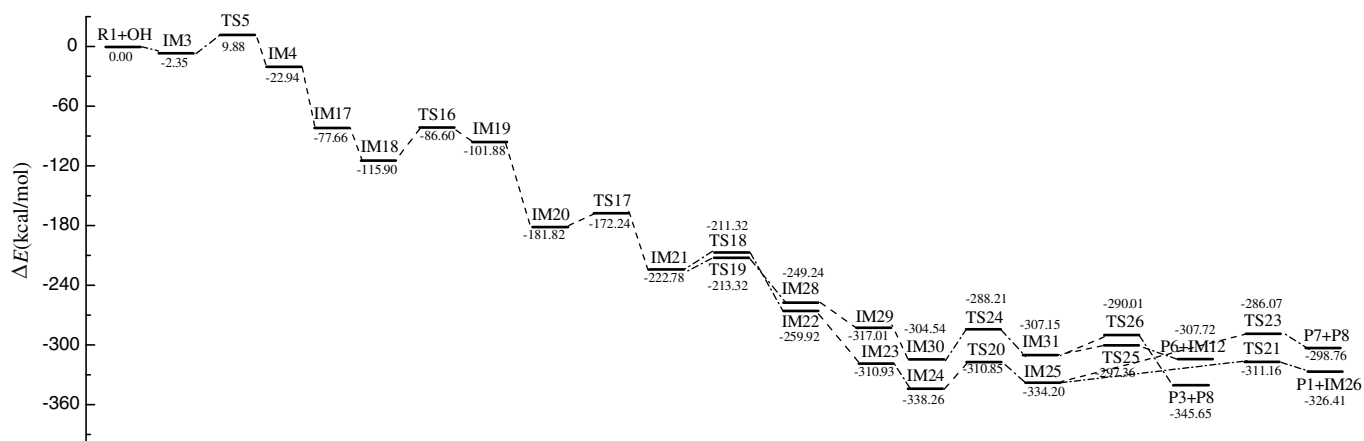
abstraction from the CH$_3$O group and abstractions of the H atoms attached to the carbon–carbon double bond.

For H abstraction from the CH$_3$O group, complex IM3 is formed first through the H-bond. The length of the H-bond (O11—H5) in IM3 is 1.828 Å which is a typical hydrogen bond length. The energy of IM3 is 2.35 kcal/mol lower than the original reactants (MVE + OH) as is demonstrated. Following this process, H6 atom is abstracted from the CH$_3$O group by the transition state TS5. The transition vector clearly shows the motion of H6 between C1 and O2. In TS5 structure, the break of C1—H6 bond is elongated by 0.105 Å, while the formation of H6—O2 bond is longer than the equilibrium value of 0.967 Å in H$_2$O by 0.429 Å. Calculations show that the energy barrier of this process is 12.23 kcal/mol. Thus, the abstraction of H6 atom can occur readily in the atmosphere. The products of H6 abstraction denoted as IM4, is an open-shell radical and will be further oxidized in atmosphere. The H6 atom abstraction is exothermic by 22.94 kcal/mol.

For the abstraction of H7 and H8 atoms attached to the carbon–carbon double bond, complexes (IM3′ and IM3″ in Fig. S1) are formed through H-bond. The energies of IM3′ and IM3″ are 2.26 and 2.03 kcal/mol, respectively, lower than the original reactants (MVE + OH). Following these processes, H7 and H8 atoms are abstracted from C2 and C3 by the transition states TS5′ and TS5″, respectively. Calculations show that the energy barriers of these two processes are 15.77 and 19.05 kcal/mol, respectively. These two processes are exothermic by 13.88 and 9.70 kcal/mol, respectively. Comparison of these three H abstraction reaction processes indicate that although the differences of energy barriers are small, the reaction heats of them have large difference. Thus, the H atoms attached to carbon–carbon double bond are less activated than the H atoms in the CH$_3$O group. Therefore, R4 and R5 are not expected to be important. This is well in agreement with the experimental study previously reported [10]. The intermediate resulted from the H abstraction process of MVE which is briefly radical intermediate, IM4. IM4 will be followed by the reaction with O$_2$/NO.

3.2. Secondary reactions

We can see from above analyses that the pathways of OH addition to the vinyl and H abstraction from CH$_3$O group are energetically favorable reaction channels for the reaction of MVE with OH radicals. IM1, IM2 and IM4 species are important radical intermediates produced in the degradation process of MVE initiated by OH radicals. In atmosphere they will further react with O$_2$/NO leading to removal.

3.2.1. Atmospheric reaction pathway of IM1

The intermediate IM1 is one energy-rich radical which can react with molecular oxygen readily to form intermediate radical IM5. The calculated profile of the potential energy surface shows that the reaction of IM4 with O$_2$ is a barrierless association. In the presence of NO, IM5 will react with NO immediately to give OH—O$_2$—NO—MVE adduct (IM6 in Fig. S2). Subsequent reaction of IM6 is a direct decomposition via the cleavage of O3—O4 bond to form intermediate, oxyl radical IM7, and NO$_2$ through transition state TS6 with an energy barrier of 26.95 kcal/mol. Further reactions of IM7 are likely to undergo three possible reactions: two decomposition reactions and one O$_2$ direct abstraction reaction. The reaction scheme is shown as follows:

IM1 + O$_2$ → IM5		$\Delta H = -53.57$ kcal/mol
IM5 + NO → IM6		$\Delta H = -30.93$ kcal/mol
IM6 → TS6 → IM7 + NO$_2$	$\Delta E = 26.95$ kcal/mol	$\Delta H = -18.53$ kcal/mol

IM7 → TS7 → IM8 + HCHO (P1)	$\Delta E = 17.49$ kcal/mol	$\Delta H = -7.53$ kcal/mol
IM8 + O$_2$ → IM9		$\Delta H = -73.80$ kcal/mol
IM9 → TS8 → P2 + HO$_2$	$\Delta E = 19.73$ kcal/mol	$\Delta H = -4.32$ kcal/mol
IM7 → TS9 → IM10	$\Delta E = 29.93$ kcal/mol	$\Delta H = -28.72$ kcal/mol
IM10 → TS10 → P3 + CH$_3$O	$\Delta E = 28.14$ kcal/mol	$\Delta H = -15.26$ kcal/mol
IM7 + O$_2$ → IM11		$\Delta H = -61.26$ kcal/mol
IM11 → TS11 → P4 + HO$_2$	$\Delta E = 19.87$ kcal/mol	$\Delta H = -29.84$ kcal/mol

One decomposition reaction is the break of C2—C3 bond to form formaldehyde P1 and methyl formate radical IM8 by passing transition state TS7 with the energy barrier value of 17.49 kcal/mol. In TS7, the bond length of C2—C3 is about 0.60 Å longer than that in IM7. Through transition state, TS8, the radical IM8 will further react with O$_2$ to give the corresponding methyl formate (P2) and HO$_2$ with an energy barrier of 19.73 kcal/mol.

The other decomposition reaction is the break of C2—O1 bond that is not directly from IM7 but from one H-transfer process. TS8 is the transition state corresponding to the H-transfer process in which H10 atom is transferred from atom O3 to O2, and the intermediate IM10 is formed (with a barrier of 29.93 kcal/mol). The rupturing of the C2—O1 bond occurs via the transition state TS10 with the energy barrier of 28.14 kcal/mol. The product of this reaction is P3 and CH$_3$O. The radical CH$_3$O will further react with O$_2$ to give the corresponding methyl formate P1 and HO$_2$. Comparing with the cleavage of C2—C3 bond, the decomposition via the break of C2—O1 bond may be ignored.

The O$_2$ direct abstraction reaction of the oxyl radical IM7 with molecular oxygen may occur. The result of the O$_2$ direct abstraction reaction is the formation of 2-hydroxy-3-oxa-butanal (P4) and HO$_2$ through transition state TS11. This process is completed through two steps. First, IM7 is attacked by O$_2$ to form the intermediate, IM11, and then HO$_2$ is removed to form P4. The calculated profile of the potential energy surface shows that the O$_2$ direct abstraction process has an energy barrier of 19.87 kcal/mol. This value means that the direct O$_2$ abstraction process is strongly competitive with the C1—C2 bond break reactions for further reaction of IM7.

Comparison of the data reveals that the reaction of C1—C2 bond break and O$_2$ direct abstraction are the more favorable pathway and competitive. Formaldehyde (P1), methyl formate (P2) and 2-hydroxy-3-oxa-butanal (P4) are the main products for the reaction of IM1 with OH radicals in the presence of O$_2$/NO. Products of C—O bond fission will be less likely to be observed in experiment.

3.2.2. Atmospheric reaction pathway of IM2

Similar to the reaction of IM1, the atmospheric reaction pathways of IM2 with O$_2$/NO are shown as follows:

IM2 + O$_2$ → IM14		$\Delta H = -72.39$ kcal/mol
IM14 + NO → IM15		$\Delta H = -20.21$ kcal/mol
IM15 → TS12 → IM10 + NO$_2$	$\Delta E = 21.59$ kcal/mol	$\Delta H = -14.01$ kcal/mol
IM10 → TS13 → IM12 + HCHO (P2)	$\Delta E = 6.55$ kcal/mol	$\Delta H = -10.36$ kcal/mol
IM10 → TS10 → P3 + CH$_3$O	$\Delta E = 19.12$ kcal/mol	$\Delta H = -28.72$ kcal/mol
IM10 + O$_2$ → IM16		$\Delta H = -74.35$ kcal/mol
IM16 → TS15 → P5	$\Delta E = 8.33$ kcal/mol	$\Delta H = -20.54$ kcal/mol

Further reactions of the oxyl radical IM10 are likely to undergo via three possible channels: two decomposition reactions and one O_2 direct abstraction reaction. One decomposition reaction is the break of C2—C3 bond to form IM12 and methyl formate (P2) by passing the transition state TS13 with the relative energy value of 6.55 kcal/mol. In TS13, the bond length of C2—C3 is 1.970 Å longer about that in IM10. Through the transition state TS14, the radical IM12 will further react with O_2 to give the corresponding formaldehyde P1 and HO_2.

The calculated results show that the other decomposition reaction via the fission of the C2—O1 bond may be ignored because the energy barrier of this process is 19.12 kcal/mol. This value is three times higher than that of C2—C3 bond cleavage.

The O_2 direct abstraction is H7 being abstracted from C2H7O13 in the oxyl radical IM10 with molecular oxygen to form glycolic acid methyl ester (P5) and HO_2 through transition state TS15. The energy barrier of TS15 is 8.33 kcal/mol indicating this direct abstraction process is strongly competitive with the decomposition reactions of C2—C3 bond cleavage.

Comparison of the above calculated results shows that the more favorable pathways for further reaction of intermediate IM10 are the break of C1—C2 bond and O_2 direct abstraction reaction. Formaldehyde (P1), methyl formate (P2) and glycolic acid methyl ester (P5) are the main products for the reaction of MVE with OH radicals. This phenomenon is in line with experimental observation.

3.2.3. Atmospheric reaction pathway of IM4

The potential energy surface of Fig. 2 shows that H abstraction from the CH_3O group of MVE is energetically feasible pathway for photochemical oxidation of MVE by OH radicals, leading to the products IM4 and H_2O. IM4 is an activated radical and will further react with molecular oxygen in atmosphere to form intermediate, IM17. Calculation shows that this process is barrierless and the enthalpy is 54.72 kcal/mol.

In the troposphere, IM17 will react with ubiquitous NO to form IM18. In IM18, the bond lengths of O3—O4 and O4—N are 1.433 and 1.482 Å. IM19 is not stable, and then a direct decomposition reaction via the cleavage of O3—O4 bond will occur subsequently. The reaction pathway scheme can be described as follows:

IM4 + O_2 → IM17		ΔH = −54.72 kcal/mol
IM17 + NO → IM18		ΔH = −38.24 kcal/mol
IM18 → TS16	ΔE = 29.30 kcal/mol	ΔH = −15.28 kcal/mol
→ IM19 + NO_2		
IM19 + O_2 → IM20		ΔH = −79.94 kcal/mol
IM20 → TS17	ΔE = 9.08 kcal/mol	ΔH = −50.04 kcal/mol
→ IM21 + HO_2		

The result of the decomposition of IM18 is to form the intermediate structure IM19 and NO_2. TS16 is the transition state corresponding to this process in which O3—O4 bond breaks while one typical H-bond forms between N1 and H4 atoms. The lengths of O3—O4 and N1—H4 are 1.813 and 1.947 Å, respectively. The energy barrier of this process is 29.30 kcal/mol. Next, a direct oxygen abstraction occurred in which the oxyl radical IM19 again react with molecular oxygen to form the intermediate IM21 (vinyl formate) and HO_2. This process is completed through two steps. Firstly, the radical IM19 is attacked by O_2 to form an intermediate IM20, and then HO_2 is removed to form IM21. The first step is a barrierless association, and the second step has a low energy barrier of 9.08 kcal/mol.

According to experimental assumptions [10], IM21 is not the final degradation product, which will further react with OH radicals through addition–elimination. In these addition processes, two sites are observed for adding the OH radical, in which one is site

C2 and the other is site C3. In both cases the products are the same, and the reaction mechanisms are similar.

The first case is that the addition site of OH radical to IM21 is on C2. The result of this addition is the formation of an intermediate, IM22, through transition state TS18. Intermediate IM23 is formed from the reaction of IM22 with O_2 through one barrierless process. Intermediate IM24 is directed from the reaction of IM23 with NO. Then unimolecular decomposition of IM24 occurred subsequently. The reaction scheme is shown as follows:

IM21 + OH	ΔE = 11.46 kcal/mol	ΔH = −48.60 kcal/mol
→ TS18 → IM22		
IM22 + O_2 → IM23		ΔH = −72.39 kcal/mol
IM23 + NO → IM24		ΔH = −20.21 kcal/mol
IM24 → TS20	ΔE = 27.41 kcal/mol	ΔH = 4.89 kcal/mol
→ IM25 + NO_2		
IM25 → TS21 → IM26	ΔE = 23.04 kcal/mol	ΔH = 10.31 kcal/mol
+ HCHO (P1)		
IM26 + O_2 → IM27		ΔH = −75.49 kcal/mol
IM27 → TS22	ΔE = 10.05 kcal/mol	ΔH = −32.99 kcal/mol
→ P6 + HO_2		
IM25 → TS23	ΔE = 48.13 kcal/mol	ΔH = −12.69 kcal/mol
→ P7 + P8		

The decomposition of IM24 produces oxyl radical IM25 and NO_2 through the transition state TS20 with a high energy barrier of 27.41 kcal/mol. IM25 is an open-shell radical and will further react by two kinds of possible bond break. The first one is the break of the C2—C3 bond leading to the formation of intermediate HCHO (P1) and IM26 through the transition state TS21. Calculation reveals that TS21 has an energy barrier of 23.04 kcal/mol. In TS21 the bond length of C2—C3 is 2.138 Å longer about 0.667 Å than that in intermediate IM25. Structure IM26 is not stable and will further react with molecular oxygen to form the final product P6 (formic anhydride) and HO_2.

The second possible bond break of IM25 is the cleavage of C2—O1 bond, forming HCO_2 (P7) and a three-membered ring compound, denoted as P8. A transition state, TS23 was associated with the decomposition process. The length for the break of the C2—O1 bond is 2.385 Å, which is longer by 0.914 Å than the equilibrium value of 1.471 Å in IM26. Calculation indicates that this decomposition has a high potential barrier of 48.13 kcal/mol, which is two times higher than that of the first decomposition. Thus, the decomposition of IM26 by the fission of C2—O1 bond may be ignored.

The second addition case of OH to IM21 is that the addition site is on C3. Similar to the first addition case, the result of this addition is the formation of intermediate IM28 through transition state TS19. Intermediate 30 is directed from the reaction of IM28 with O_2 through one barrierless process. Intermediate IM30 is directed from the reaction of IM29 with NO. The following process is also the break of C2—C3 bond. The reaction scheme is depicted as follows:

IM21 + OH	ΔE = 9.46 kcal/mol	ΔH = −35.92 kcal/mol
→ TS19 → IM28		
IM28 + O_2 → IM29		ΔH = −55.30 kcal/mol
IM29 + NO → IM30		ΔH = −30.66 kcal/mol
IM30 → TS24	ΔE = 22.33 kcal/mol	ΔH = −18.94 kcal/mol
→ IM31 + NO_2		
IM31 → TS25	ΔE = 9.79 kcal/mol	ΔH = −10.36 kcal/mol
→ IM12 + P6		
IM31 → TS26	ΔE = 17.14 kcal/mol	ΔH = −55.64 kcal/mol
→ P3 + P8		

The result of the break of C2—C3 bond is the formation of final product P6 (formic anhydride) and CH_2OH (IM12) through the transition state TS25 with an energy barrier of 9.79 kcal/mol. Then IM12 will be changed as P1 through its reaction with O_2.

The possible decomposition of IM31 via cleavage of the C2—O1 bond is also studied in this work. This decomposition leads to the formation of P3 (glycolaldehyde) and P8. A transition state, TS26, was identified associated with the decomposition. The length for the breaking C2—O1 bond is 1.906 Å, which is longer by 0.320 than the equilibrium value of 1.586 Å in IM32. Calculations indicate that this decomposition has an energy barrier of 17.14 kcal/mol. Different from the decomposition of IM25 via the break of C2—O1 bond, the decomposition of IM31 by the cleavage of C2—O1 bond is strongly competitive with the break of C2—C3 bond. P8 (HCO_2) will further react with O_2 to form CO_2.

The above analyses show that H abstraction product, vinyl formate, will again react with OH radical to form formaldehyde (P1) and formic anhydride (P6). P1 and P6 are expected to be only of minor importance.

4. Conclusions

A theoretical study of the OH-initiated atmospheric photooxidation reaction of methyl vinyl ether has been carried out by the use of DFT calculations. The following conclusions can be drawn as a result of our data:

1. The reaction of MVE with OH radicals proceeds via two possible mechanisms:
   (1) The first mechanism is addition–elimination. There are two additional modes for OH radicals because there are two C atoms (C2 and C3 atoms) in vinyl. The most energetically favorable reaction pathway is that of OH addition to the terminal carbon positions (C3 atom).
   (2) The second mechanism corresponds to the H abstraction reaction. The H abstraction from the CH_3O group of MVE can occur readily.
2. Formic anhydride (H abstraction product) will again react with OH radicals and lead to the formation of formaldehyde (P1) and formic anhydride (P6). However, they are expected be only of very minor importance.

3. The main products of the OH-initiated atmospheric photooxidation of MVE are formaldehyde (P1) methyl formate (P2) and glycolic acid methyl ester (P5). Formaldehyde (P1) methyl formate (P2) is mainly from the OH addition reaction to terminal carbon positions (C3 atom).

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2008.08.006.

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