

Mechanism of OH-initiated atmospheric photooxidation of the organophosphorus insecticide (C₂H₅O)₃PS

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ARTICLE INFO

Article history:

Received 17 November 2008

Received in revised form

4 May 2009

Accepted 25 May 2009

Keywords:

TEPT

OH radicals

Atmospheric photooxidation

Reaction mechanism

Quantum chemical study

ABSTRACT

O,O,O-triethyl phosphorothioate ((C₂H₅O)₃PS, TEPT) is a widely used organophosphorus insecticide. TEPT may be released into the atmosphere where it can undergo transport and chemical transformations, which include reactions with OH radicals, NO₃ radicals and O₃. The mechanism of the atmospheric reactions of TEPT has not been fully understood due to the short-lifetime of its oxidized radical intermediates, and the extreme difficulty in detection of these species experimentally. In this work, we carried out molecular orbital theory calculations for the OH radical-initiated atmospheric photooxidation of TEPT. The profile of the potential energy surface was constructed, and the possible channels involved in the reaction are discussed. The theoretical study shows that OH addition to the P=S bond and H abstractions from the CH₃CH₂O moiety are energetically favorable reaction pathways. The dominant products TEP and SO₂ arise from the secondary reactions, the reactions of OH-TEPT adducts with O₂. The experimentally uncertain dominant product with molecular weight 170 is mostly due to (C₂H₅O)₂P(S)OH and not (C₂H₅O)₂P(O)SH.

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1. Introduction

Organophosphorus pesticides (OPs) were introduced to substitute for organochlorine pesticides and other chlorinated hydrocarbon pesticides because they have the ability to degrade faster and more easily in the environment (Chambers, 1992; Jaga and Dharmani, 2003). OPs have been used in agricultural and household pest control for more than 40 years (Karczmar, 1970). Due to their widespread use, serious environmental problems are emerging, and they pose an important risk to human health (Westlake et al., 1981; McInnes et al., 1996; Hai et al., 1997; Kawahara et al., 2005). OPs belong to the most toxic chemicals in the world (Levin and Rodnitzky, 1976; Donarski et al., 1989; Kwong, 2002). They are responsible for 80% of pesticide-related hospitalizations (Taylor, 2001) and sometimes cause death. In the modern age, nearly everyone is, or has been, exposed to OPs in their home or work environment (Barr et al., 2004).

Pesticides and their precursors may enter the atmosphere as drift during spraying crops or from deposited residue by volatilization and wind erosion where they can undergo transport and chemical transformations (Glötfelty et al., 1990; Van den Berg et al., 1999). Organophosphorus pesticides have been frequently observed in the atmosphere, especially in rain and air in urban and agricultural areas (Coupe et al., 2000; Yao et al., 2008). The frequency of

detection in air samples is more than 50% in Mississippi (Coupe et al., 2000). Analysis of particle- and gas-phase fractions of air samples revealed that most OPs exist mainly in the gas phase under the atmospheric conditions (Yao et al., 2008). This has greatly increased the potential for human exposure to these highly toxic materials. To assess the atmospheric behavior of pollutants, it is critical to understand their atmospheric reactions. OH radicals play the most central role in determining the oxidation power of the atmosphere. The reactions initiated by OH radicals have been regarded as the dominant atmospheric loss process of many pesticides (Tuazon et al., 1986; Atkinson et al., 1988; Goodman et al., 1988). Despite their importance, the OH radical-initiated atmospheric reactions of organophosphorus pesticides have received relatively little attention.

In several studies, O,O,O-triethyl phosphorothioate ((C₂H₅O)₃PS, TEPT) was selected as a “model” alkyl organophosphorus pesticide (Verschoyle and Cabral, 1982; Zhang et al., 2002; Basheer et al., 2007). Two experimental studies are on record for the reaction of TEPT with OH radicals. In 2006, Aschmann and Atkinson (2006) measured the rate constants using relative rate methods at the normal atmospheric pressure over the temperature range of 296–348 K, and reported the Arrhenius expression. Since TEPT contains a P=S bond, it is highly reactive toward OH radicals, but reacts only slowly with NO₃ radicals and O₃. The calculated atmospheric lifetimes are 0.7–1.8 h, 23–45 days and >275 days, respectively. In 2007, Tuazon and his coworkers (Tuazon et al., 2007) used *in situ* atmospheric pressure ionization tandem mass

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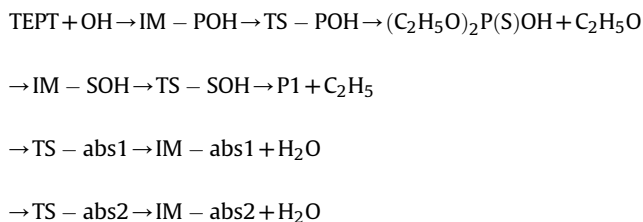
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spectrometry (API-MS), gas chromatography (GC) and *in situ* Fourier transform infrared spectroscopy (FT-IR) to investigate the products formed from the OH radical-initiated reaction of TEPT. The dominant products observed are $(\text{C}_2\text{H}_5\text{O})_3\text{PO}$ (TEP, 54–62% yield), SO_2 ($67 \pm 10\%$ yield), CH_3CHO (22–40% yield) and one uncertain compound. The API-MS analyses indicate that the molecular weight of this uncertain product is 170, and it was attributed to $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{SH}$ or $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{S})\text{OH}$. Possible reaction mechanisms were proposed to explain the observed products. However, there is a shortage of direct experimental data associated with the reaction mechanism, largely due to the lack of efficient detection schemes for radical intermediate species.

Quantum calculation is especially suitable for establishing the feasibility of a reaction pathway. In this paper, we have carried out a theoretical study on the OH radical-initiated atmospheric photooxidation reaction of TEPT in order to find favorable reaction pathways and sites. Possible secondary reaction pathways were also studied to find the formation mechanism of secondary pollutants from the OH radical-initiated atmospheric reaction of TEPT. Elucidation of the reaction mechanism is very challenging due to its inherent complexity. The potential energy surface is useful to explain the experimentally observed branching ratios, thermochemical properties, and rate coefficients.

2. Computational method

High-accuracy molecular orbital calculations were carried out for the OH radical-initiated atmospheric photooxidation of TEPT.



The Gaussian 03 package (Frisch et al., 2003) was used on an SGI Origin 2000 supercomputer. The geometrical parameters of reactants, transition states, intermediates and products were optimized at the MPWB1K (Becke, 1996; Adamo and Barone, 1998; Zhao and Truhlar, 2004) level with a standard 6-31G(d,p) basis set. The MPWB1K method that is based on the modified Perdew and Wang 1991 exchange functional (Perdew, 1991) and Becke's 1995 meta correlation functional (Becke, 1996) is a hybrid density functional theory (HDFT) model with excellent performance for thermochemistry, thermochemical kinetics, hydrogen bonding and weak interactions. Furthermore, previous study shows that MPWB1K is an excellent method for prediction of transition state geometries (Zhao and Truhlar, 2004). The mean unsigned errors (MUEs) of transition state geometries optimized at the MPWB1K level, which are the averages of the absolute deviations of calculated values from database values, are 0.02 Å for the five reactions in the SPG15/01 database (Zhao and Truhlar, 2004). The vibrational frequencies were also calculated at the MPWB1K/6-31G(d,p) level in order to determine the nature of the stationary points, the zero-point energy (ZPE), and the thermal contributions to the free energy of activation. Each transition state was verified to connect the designated reactants with products by performing an intrinsic reaction coordinate (IRC) analysis (Fukui, 1981). For a more accurate

evaluation of the energetic parameters, a more flexible basis set, 6-311 + G(3df,2p), was employed to determine the energies of the various species. The profile of the potential energy surface was constructed at the MPWB1K/6-311 + G(3df,2p)//MPWB1K/6-31G(d,p) level including ZPE correction.

3. Results and discussion

Due to the absence of experimental information on the thermochemical parameters for the present reaction system, it is difficult to make a direct comparison of the calculated results with experimental data. Thus, we optimized the geometries of $(\text{CH}_3\text{O})_3\text{PO}$, PS and CH_3CHO . The calculated results at the MPWB1K/6-31G(d,p) level agree well with the available experimental values (Hollenstein and Gunthard, 1971; Huber and Herzberg, 1979; Van Wazer and Ewig, 1986) and the maximum relative error is less than 2.0%.

3.1. The reaction of TEPT with OH radicals

Addition of OH to the P=S bond is a possible pathway for the reaction of TEPT with OH radicals. Since OH is a strongly nucleophilic radical, H abstraction from the alkyl group in TEPT should be another possible reaction pathway. Altogether, four possible reaction pathways, R1–R4, were identified. The profile of the potential energy surface for the reaction of TEPT with OH radicals is shown in Fig. 1. The reaction scheme can be described as follows:

- R1 association–elimination
- R2 association–elimination
- R3 H abstraction from –CH₂– group
- R4 H abstraction from –CH₃ group

3.1.1. Association–elimination pathways

The association–elimination pathways are analyzed first. Two different adduct isomers, addition of the OH radical to the P atom (denoted IM-POH) and addition of OH to the S atom (denoted IM-

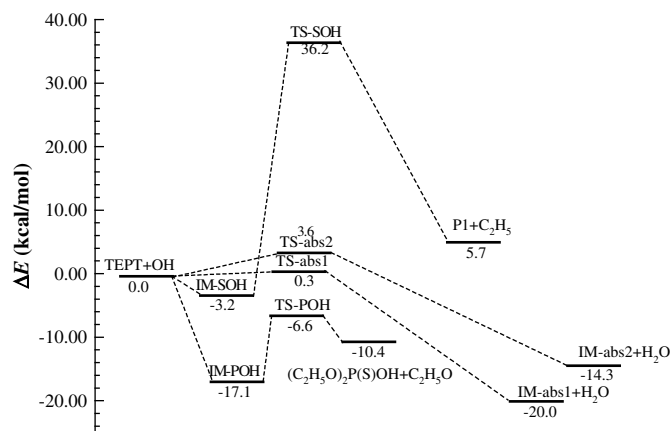


Fig. 1. Profile of the potential energy surface for the reaction of TEPT with OH radicals at the MPWB1K/6-311 + G(3df,2p) level.

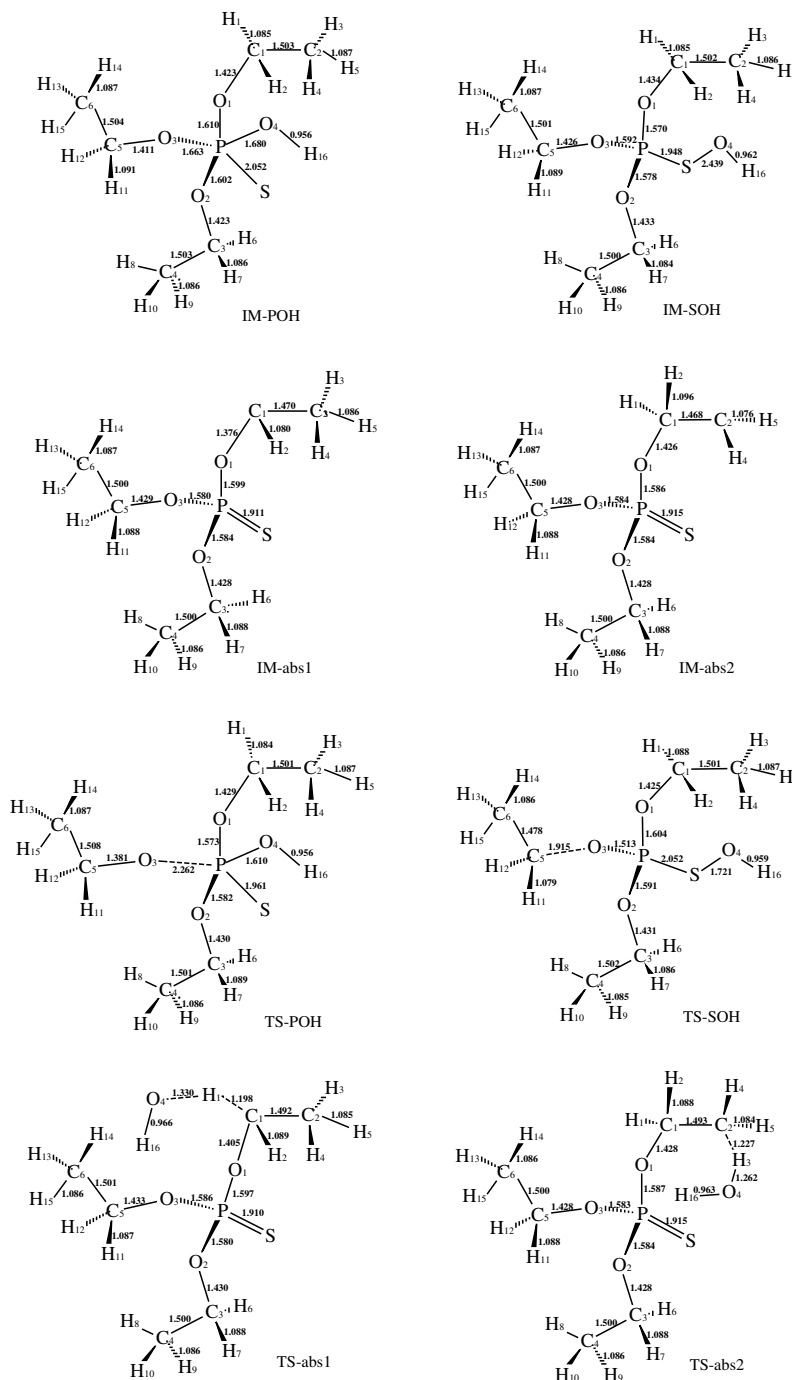


Fig. 2. MPWB1K/6-31G(d,p) optimized geometries for the reactant, intermediates, transition states and products involved in the reaction of TEPT with OH radicals. Distances are in angstroms.

SOH), were formed. Thus, two reaction pathways, R1 and R2, are possible for addition of OH to the P=S double bond in TEPT. Calculations show that the addition is a barrierless association. The geometrical parameters of IM-POH and IM-SOH are shown in Fig. 2. It is interesting to compare the relative stability of the two OH-TEPT adducts. The energy of IM-POH is 13.9 kcal mol⁻¹ lower than that of IM-SOH at the MPWB1K/6-311 + G(3df,2p) level. The addition of OH to the P=S double bond of TEPT is a strongly exothermic process. The energies of IM-POH and IM-SOH are 17.1 and 3.2 kcal mol⁻¹ lower than the total energy of the original reactants (TEPT and OH), respectively. The high reaction energies are retained as the internal energy of the adducts. The energy-rich adducts, IM-

POH and IM-SOH, can react via unimolecular decomposition and/or with atmospheric O₂.

Unimolecular decomposition of IM-POH results in the products (C₂H₅O)₂P(S)OH and C₂H₅O via an apparent barrier, 10.4 kcal mol⁻¹, at the MPWB1K/6-311 + G(3df,2p) level. The total energies of (C₂H₅O)₂P(S)OH and C₂H₅O are 10.4 kcal mol⁻¹ lower than the total energy of the original reactants (TEPT and OH). This process would occur readily under general atmospheric conditions. (C₂H₅O)₂P(S)OH and C₂H₅O should be possible products for the reaction of TEPT with OH radicals. One dominant product with molecular weight 170 was experimentally observed in the chamber in which the OH radical-initiated oxidation reaction of TEPT was simulated

under general atmospheric conditions. The molecular weight of $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{S})\text{OH}$ is 170. $\text{C}_2\text{H}_5\text{O}$ radicals will subsequently be oxidized by O_2 to yield CH_3CHO , which was identified and quantified (22–40% yield) in the reaction chamber (Tuazon et al., 2007). CH_3CHO can not only participate in HO_x production, but also produce PA-radicals and is thus an important precursor for PAN in the atmosphere.

The unimolecular decomposition of IM-SOH with cleavage of the $\text{C}_5\text{--O}_3$ bond results in the formation of P1 [$(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{SOH}$] and C_2H_5 radical via the transition state TS-SOH. Fig. 1 shows that this process has a high barrier of $39.4 \text{ kcal mol}^{-1}$ and is endothermic by $8.9 \text{ kcal mol}^{-1}$ at the MPWB1K/6-311 + G(3df,2p) level. Thus, this decomposition process is energetically unfavorable. In the troposphere, IM-SOH will mainly be removed by reaction with O_2 .

The formation of $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{SH}$ (molecular weight 170) via the association–elimination mechanism was also investigated. The formation of $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{SH}$ from the decomposition of IM-POH involves H_{16} -migration from O_4 to S and cleavage of the P--O_3 bond. The potential barrier of H_{16} -migration is $28.1 \text{ kcal mol}^{-1}$ at the MPWB1K/6-311 + G(3df,2p) level. Thus, the direct formation of $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{SH}$ from IM-POH is energetically unfavorable. Similarly, there is no energetically feasible formation pathway for $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{SH}$ from the decomposition of IM-SOH.

3.1.2. H-abstraction pathways

Two kinds of H atoms exist in TEPT structure. Therefore, two primary pathways, R3 and R4, were identified: H abstraction from the $-\text{CH}_2-$ group, and H abstraction from the $-\text{CH}_3$ group.

H abstraction from the $-\text{CH}_2-$ moiety proceeds via the transition state TS-abs1. The structures of TS-abs1 are shown in Fig. 2. The transition vector clearly shows the motion of H_1 between C_1 and O_4 ,

with an imaginary frequency of $1119i \text{ cm}^{-1}$. This H-abstraction reaction has a low potential barrier of $0.3 \text{ kcal mol}^{-1}$ and is strongly exothermic by $20.0 \text{ kcal mol}^{-1}$ at the MPWB1K/6-311 + G(3df,2p) level.

H abstraction from the $-\text{CH}_3$ group requires crossing a barrier of $3.6 \text{ kcal mol}^{-1}$ and is strongly exothermic by $14.3 \text{ kcal mol}^{-1}$. Comparison of the two H-abstraction channels shows that the H abstraction from the $-\text{CH}_2-$ group is easier than the H abstraction from the $-\text{CH}_3$ group. This indicates that the H atoms in the $-\text{CH}_2-$ group are more activated than the H atoms in the $-\text{CH}_3$ group. H abstractions from the alkyl group in TEPT can occur readily and are expected to play an important role for the OH radical-initiated degradation of TEPT in the atmosphere. The products, denoted IM-abs1 and IM-abs2, are open-shell activated radicals and will be further oxidized in the atmosphere.

3.2. Secondary reactions

The discussion above shows that OH addition to the $\text{P}=\text{S}$ bond and H abstractions from the $\text{CH}_3\text{CH}_2\text{O}$ moiety are energetically favorable reaction pathways for the reaction of TEPT with OH radicals. IM-POH, IM-SOH, IM-abs1 and IM-abs2 are important intermediates produced in the degradation process of TEPT initiated by OH radicals. The conventional view is that these radical intermediates could be oxidized further by ubiquitous O_2 or O_2/NO and removed from the troposphere. Published work (Aschmann and Atkinson, 2006; Tuazon et al., 2007) on the products of oxidation of TEPT in smog chambers via hydroxyl chemistry supports this point. Several important secondary pollutants are produced from the reactions of IM-POH, IM-SOH, IM-abs1 and IM-abs2 with O_2 or O_2/NO .

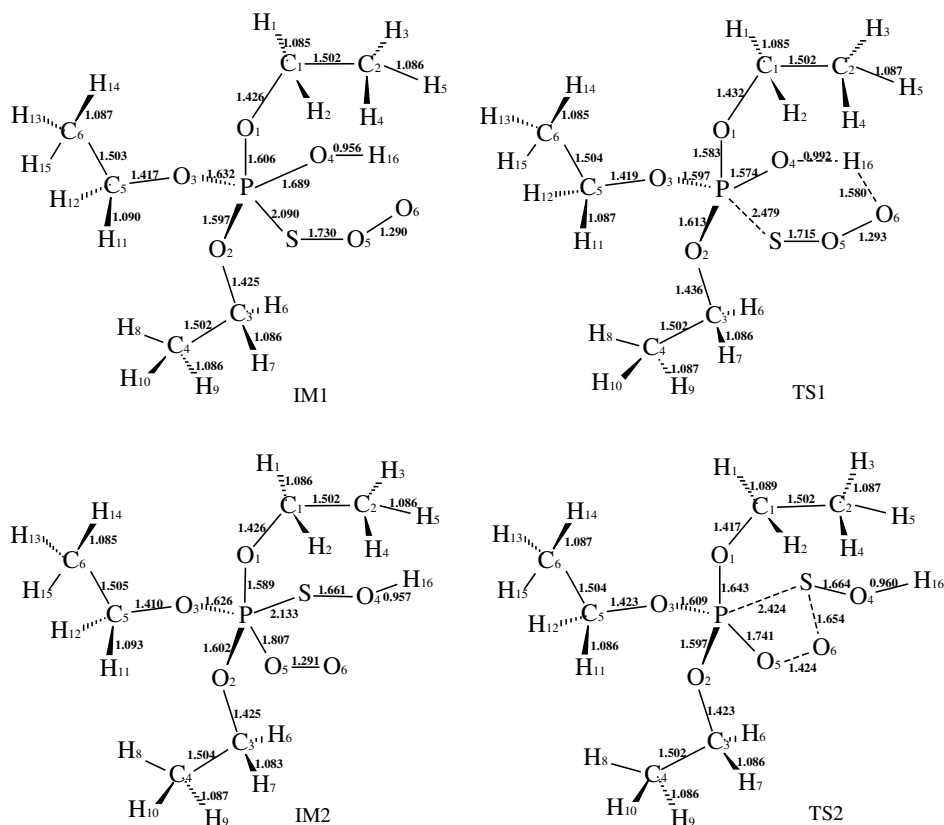


Fig. 3. MPWB1K/6-31G(d,p) optimized geometries for the intermediates, transition states and products involved in the secondary reactions of OH-TEPT adducts, IM-POH and IM-SOH, with O_2 . Distances are in angstroms.

(TEP) and SOOH. TS1 represents the transition state for this unimolecular decomposition. The potential barrier of this decomposition is 9.1 kcal mol⁻¹. The process is strongly exothermic by 24.8 kcal mol⁻¹. Similarly, the other OH-TEPT adduct, IM-SOH, can also be oxidized by O₂ in the atmosphere to produce TEP and HOSO. The reaction pathway scheme can be clarified as follows.

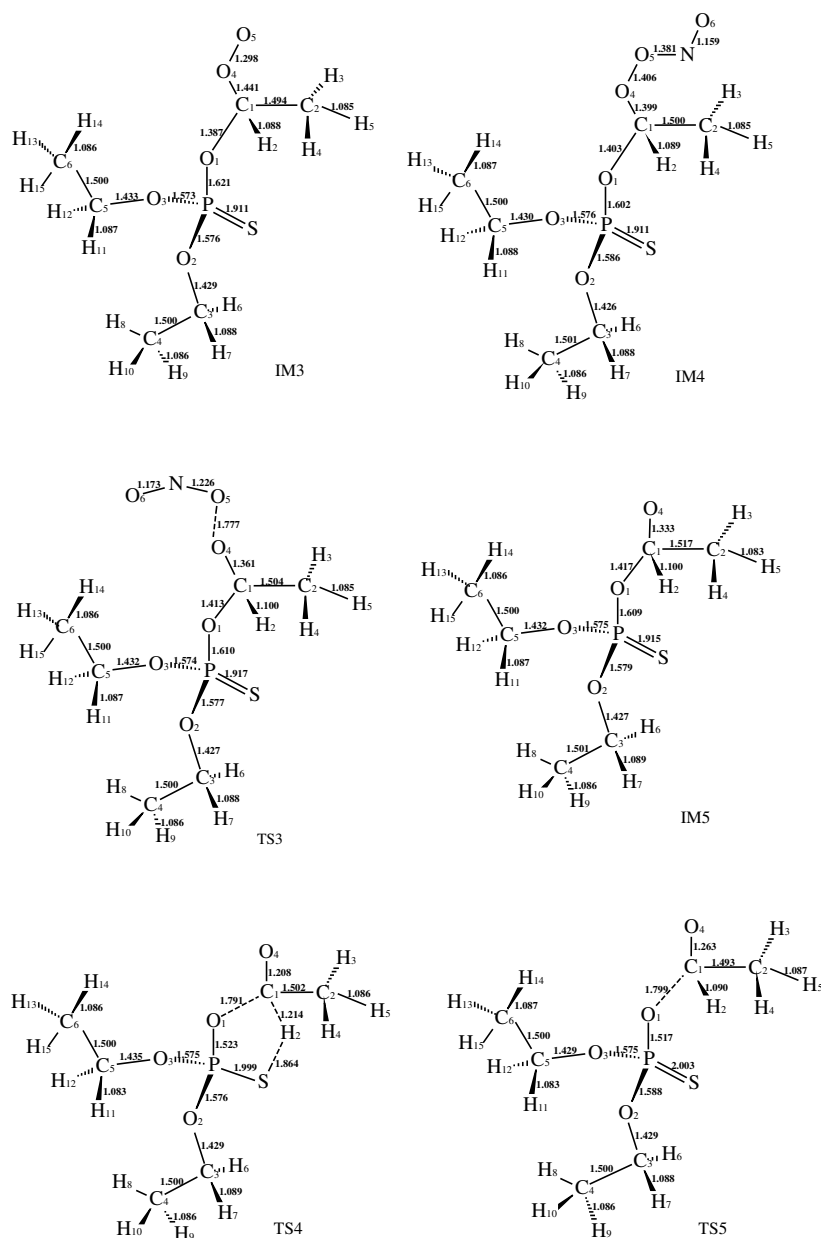
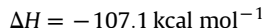


Fig. 4. MPWB1K/6-31G(d,p) optimized geometries for the intermediates, transition states and products involved in the secondary reactions of IM-abs1 with O₂/NO. Distances are in angstroms.

The study above shows that the formation of $(\text{C}_2\text{H}_5\text{O})_3\text{PO}$ (TEP) would occur readily from the OH radical-initiated atmospheric reaction of TEPT. TEP was detected in the chamber with a high formation yield (54–62%) (Tuazon et al., 2007). TEP is a harmful substance with narcotic effects and certain neurotoxic properties. It has relatively high vapor pressure and is subject to long-range air transportation. And also it can further react with OH, O_3 and NO_3 . A recent study (Aschmann et al., 2008) shows that new particle formation occurs from the reaction of TEP with OH radicals. Assuming that the aerosol had the same density as the organophosphorus reactant, the aerosol yield, defined as {(aerosol formed, corrected for wall losses)/(organophosphorus compound reacted)}, is estimate to be 6%.

SOOH and HOSO are activated radicals and will subsequently be oxidized by O_2 to yield SO_2 , which was identified and quantified (67% yield) in the reaction chamber (Tuazon et al., 2007). TEP and

SO_2 are formed from one reaction pathway, the oxidation of OH-TEPT adducts, which is in accordance with the experimental observation that the formation of TEP is accompanied by the formation of SO_2 (Tuazon et al., 2007). Interestingly, the yield of TEP (54–62%) from the OH radical-initiated atmospheric reaction of TEPT is less than that of SO_2 (67%) (Tuazon et al., 2007). This is due to the further reaction of TEP with OH, O_3 and NO_3 .

3.2.2. Atmospheric reaction pathway of IM-abs1

H abstraction from the $-\text{CH}_2-$ group of TEPT is the energetically feasible reaction pathway for photochemical oxidation of TEPT initiated by OH radicals, leading to the products IM-abs1 and H_2O . IM-abs1 is an activated radical and can further react with the ubiquitous oxygen molecules in the atmosphere to form an organic peroxy radical, IM3, via a barrierless association. The process is

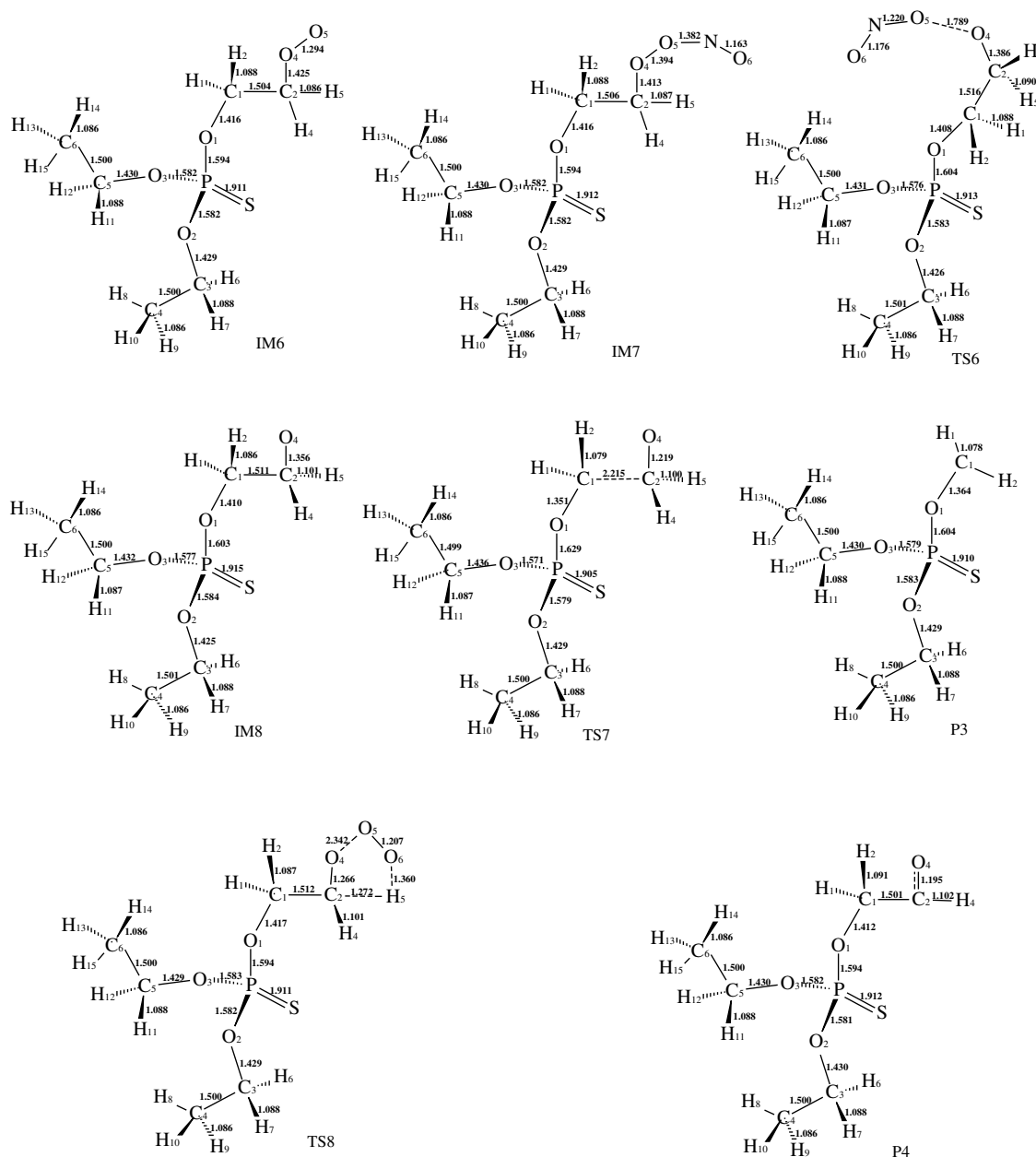
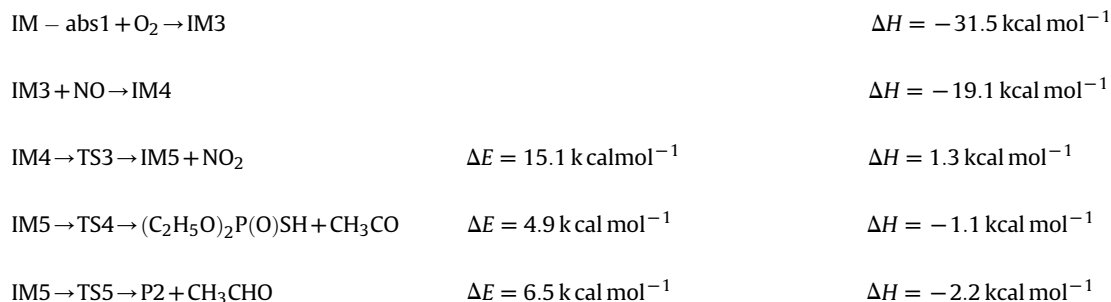


Fig. 5. MPWB1K/6-31G(d,p) optimized geometries for the intermediates, transition states and products involved in the secondary reactions of IM-abs2 with O_2/NO . Distances are in angstroms.

strongly exothermic by $31.5 \text{ kcal mol}^{-1}$. In the troposphere, IM3 will react immediately with ubiquitous NO. The entrance channel of the reaction is exoergic, leading to a vibrationally excited intermediate (denoted IM4), which promptly reacts via unimolecular decomposition. The equilibrium structure of IM4 is illustrated in Fig. 4. The reaction scheme can be described as follows:



Unimolecular decomposition of IM4 occurs via cleavage of the $\text{O}_4\text{--O}_5$ bond, forming NO_2 and an alkoxy radical IM5. A transition state, TS3, was identified as associated with the decomposition. Calculations indicate that this process has an apparent potential barrier of $15.1 \text{ kcal mol}^{-1}$ and is endothermic by $1.3 \text{ kcal mol}^{-1}$ at the MPWB1K/6-311 + G(3df,2p) level. Two possible decomposition channels were found from IM5. The first one results in the products $(\text{C}_2\text{H}_5\text{O})_2\text{P(O)SH}$ and CH_3CO via the transition state TS4. This process involves H_2 -migration and cleavage of the $\text{C}_1\text{--O}_1$ bond. The energy of TS4 is $4.9 \text{ kcal mol}^{-1}$ higher than that of IM5. It is well known that the CH_3CO radical reacts with O_2 to produce acetylperoxy radical, which can further react with NO_2 to form the relatively stable peroxyacetyl nitrate (PAN). Another main product initiated from CH_3CO with O_2 is HCHO . HCHO is a highly lachrymatory, odorous, and physiologically active substance and is classified as a typical toxic gas species in the atmosphere. Low-level HCHO injures the eyes, nose, and respiratory organs and causes allergies, which is called sick house syndrome. The other unimolecular decomposition of IM5 occurs by cleavage of the $\text{C}_1\text{--O}_1$ bond to form P2 and CH_3CHO via the transition state TS5. This process has an apparent barrier of $6.5 \text{ kcal mol}^{-1}$. The $\text{C}_1\text{--O}_1$ bond fission is exothermic by $2.2 \text{ kcal mol}^{-1}$.

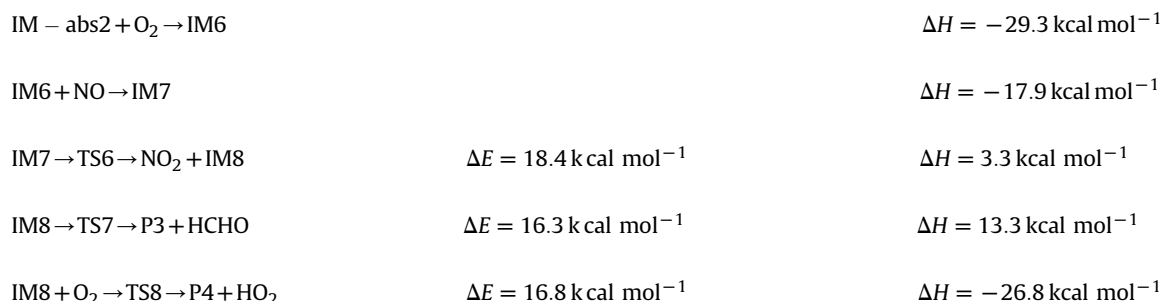
One uncertain dominant product with molecular weight 170 was observed by Tuazon and his coworkers (Tuazon et al., 2007) in the chamber in which the OH radical-initiated oxidation reaction of TEPT was simulated under general atmospheric conditions. The molecular weight 170 product has a formula of $\text{C}_4\text{H}_{11}\text{O}_3\text{PS}$ and can be attributed to $(\text{C}_2\text{H}_5\text{O})_2\text{P(O)SH}$ or $(\text{C}_2\text{H}_5\text{O})_2\text{P(S)OH}$. FT-IR

spectrometry cannot conclusively determine the product due to interferences from other products, including diethyl phosphate (a product from the OH radical reaction with TEPT). Tuazon et al. (2007) suggested that the formation of $(\text{C}_2\text{H}_5\text{O})_2\text{P(O)SH}$ or $(\text{C}_2\text{H}_5\text{O})_2\text{P(S)OH}$ arises from an association–elimination process: $\text{OH} + (\text{C}_2\text{H}_5\text{O})_3\text{PS} \leftrightarrow (\text{C}_2\text{H}_5\text{O})_3\text{P(S)OH} \rightarrow \text{C}_2\text{H}_5\text{O} + (\text{C}_2\text{H}_5\text{O})_2\text{P(O)SH}$

or $(\text{C}_2\text{H}_5\text{O})_2\text{P(S)OH}$, or arises after H abstraction from the $-\text{CH}_2-$ group in TEPT, followed by reactions with O_2/NO .

Our study shows that $(\text{C}_2\text{H}_5\text{O})_2\text{P(S)OH}$ arises from the association–elimination mechanism, and $(\text{C}_2\text{H}_5\text{O})_2\text{P(O)SH}$ arises after H abstraction from the $-\text{CH}_2-$ group in TEPT, followed by reactions with O_2/NO . The formation of $(\text{C}_2\text{H}_5\text{O})_2\text{P(S)OH}$ involves a barrierless elementary process and an elementary process with a potential barrier of $10.4 \text{ kcal mol}^{-1}$. The formation of $(\text{C}_2\text{H}_5\text{O})_2\text{P(O)SH}$ involves five elementary processes: two barrierless elementary processes and three elementary processes with apparent potential barriers. The highest barrier involved in the formation of $(\text{C}_2\text{H}_5\text{O})_2\text{P(O)SH}$ is more than 15 kcal mol^{-1} at the MPWB1K/6-311 + G(3df,2p) level. Thus, the formation of $(\text{C}_2\text{H}_5\text{O})_2\text{P(S)OH}$ is preferred over the formation of $(\text{C}_2\text{H}_5\text{O})_2\text{P(O)SH}$. The conversion from $(\text{C}_2\text{H}_5\text{O})_2\text{P(S)OH}$ to $(\text{C}_2\text{H}_5\text{O})_2\text{P(O)SH}$ requires crossing a large activation barrier of $26.8 \text{ kcal mol}^{-1}$. In addition, the energy of $(\text{C}_2\text{H}_5\text{O})_2\text{P(O)SH}$ is $3.3 \text{ kcal mol}^{-1}$ higher than that of $(\text{C}_2\text{H}_5\text{O})_2\text{P(S)OH}$ suggesting that $(\text{C}_2\text{H}_5\text{O})_2\text{P(O)SH}$ is less stable than $(\text{C}_2\text{H}_5\text{O})_2\text{P(S)OH}$. Therefore, we suggest the experimentally uncertain compound with molecular weight 170 is mostly due to $(\text{C}_2\text{H}_5\text{O})_2\text{P(S)OH}$ and not $(\text{C}_2\text{H}_5\text{O})_2\text{P(O)SH}$. Further direct experimental observation would be anticipated to verify the conclusion.

O,O-diethyl methylphosphonothioate ($(\text{C}_2\text{H}_5\text{O})_2\text{P(S)CH}_3$, DEMPT) is also a widely used organophosphorus insecticide. The dominant atmospheric loss process of DEMPT is by the gas-phase reaction with OH radicals. Products were investigated by Tuazon and his coworker (Tuazon et al., 2007). Similar to the OH radical-



initiated reaction of TEPT, an uncertain dominant product with molecular weight 140 was observed by Tuazon and his coworkers (Tuazon et al., 2007) in the chamber in which the OH radical-initiated atmospheric reaction of DEMPT was simulated. The molecular weight 140 product has a formula of $C_2H_5O_2PS$ and can be attributed to $C_2H_5OP(O)(CH_3)SH$ or $C_2H_5OP(S)(CH_3)OH$. According to the mechanism of the OH radical-initiated oxidation reaction of TEPT, we suggest the experimentally uncertain compound with molecular weight 140 is mostly due to $C_2H_5OP(S)(CH_3)OH$ and not $C_2H_5OP(O)(CH_3)SH$.

3.2.3. Atmospheric reaction pathway of IM-abs2

The atmospheric reaction pathways of IM-abs2 with O_2/NO are similar to the reactions of IM-abs1. The equilibrium structures of intermediates, transition states and products involved in the atmospheric reaction pathways of IM-abs2 with O_2/NO are illustrated in Fig. 5. The results show that the removal reaction of IM-abs2 with O_2/NO is more favored than its unimolecular decomposition. The reaction scheme is shown as follows:

4. Conclusions

The atmospheric oxidation of TEPT was investigated theoretically by high-accuracy molecular orbital calculations. The study shows that OH addition to the $P=S$ bond and H abstractions from the CH_3CH_2O moiety are energetically favorable reaction pathways. The dominant products TEP and SO_2 arise from the secondary reactions, the atmospheric reactions of OH-TEPT adducts with O_2 . $(C_2H_5O)_2P(S)OH$ arises from the association–elimination mechanism, and $(C_2H_5O)_2P(O)SH$ arises after H abstraction from the $-CH_2-$ group in TEPT, followed by reactions with O_2/NO . The formation of $(C_2H_5O)_2P(S)OH$ is preferred over the formation of $(C_2H_5O)_2P(O)SH$. Therefore, we suggest the experimentally uncertain compound with molecular weight 170 is mostly due to $(C_2H_5O)_2P(S)OH$ and not $(C_2H_5O)_2P(O)SH$. Under the general atmospheric conditions, the OH radical-initiated atmospheric photooxidation of TEPT would occur readily. Unfortunately, several degradation products have some direct or indirect harmful effects on the environment and the human health.

Acknowledgements

This work was supported by NSFC (National Natural Science Foundation of China, project No. 20737001, 20777047), Shandong Province Outstanding Youth Natural Science Foundation (project No. JQ200804) and the Research Fund for the Doctoral Program of Higher Education of China (project No. 200804220046). The authors thank Dr. Pamela Holt for proofreading the manuscript.

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