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Unexpected malformations in
Xenopus tropicalis



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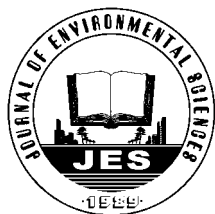
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Mechanism and kinetic properties of NO₃-initiated atmospheric degradation of DDT

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ABSTRACT

In this article, the NO₃ radical-initiated atmospheric oxidation degradation of DDT was theoretically investigated using molecular orbital theory calculations. All the calculations of intermediates, transition states and products were performed at the MPWB1K/6-311+G(3df,2p)//MPWB1K/6-31+G(d,p) level of theory. Several energetically favorable reaction pathways were revealed. The formation mechanisms of secondary pollutants were presented and discussed. The rate constants were deduced over the temperature range of 273–333 K using canonical variational transition-state (CVT) theory with the small curvature tunneling (SCT) method. Our study shows that H abstraction from the alkyl group and NO₃ addition to the C₃ atom of the benzene ring are the dominant reaction pathways. The rate-temperature formula of the overall rate constants is $k(T)(\text{DDT}+\text{NO}_3) = (7.21 \times 10^{-15})\exp(-153.81/T) \text{ cm}^3/(\text{mol}\cdot\text{sec})$ over the possible atmospheric temperature range of 273–333 K. The atmospheric lifetime of DDT determined by NO₃ radical is about 52.5 days, which indicates that it can be degraded in the gas phase within several months.

Introduction

Dichlorodiphenyltrichloroethane (DDT) is a synthetic insecticide which belongs to the family of chemically related organochlorine pesticides. DDT had been used widely all over the world. More than 270,000 ton DDT was produced between 1952 and 1983 in China (Li et al., 1999). The increasing use of synthetic chemical pesticides has caused worldwide pollution. The significant problems of human illness and death that follow the occupational or accidental exposure to DDT have been well documented (Henriques et al., 1997; Rusiecki et al., 2005; Cojn et al., 2007). The LC₅₀ value shows that DDT has a highly acute toxicity (Zhou et al., 2011; Lotofo et al., 2001). Thus, DDT had been banned in many countries. However, DDT is still used for some purposes, such as malaria control, because it is cost effective, easily available, and displays a wide spectrum of bioactivity. In addition, DDT has a long half-

life in the environment. Thus, high concentrations in the environment are still observed (Jaward et al., 2005; Qiu et al., 2004; Louie and Sin, 2003).

DDT can enter the atmosphere as drift during spraying of crops or from deposited residue by volatilization and wind erosion, where it can undergo transport and chemical transformations (Spencer and Cliath, 1972). It has been frequently observed in the atmosphere. For example, the high atmospheric concentration of 394 pg/m³, was reported at Taihu, China (Qiu et al., 2004). The average air concentration of DDT around the Great Lakes was found to be 38 pg/m³ (McConnell et al., 1988). Analysis of particle- and gas-phase fractions of air samples revealed that DDT exists mainly in the gas phase under general atmospheric conditions (Naudé and Rohwer, 2012). This has greatly increased the potential for human exposure to the highly toxic pesticide. Particle-phase DDT may be removed from the atmosphere through dry or wet deposition. The tropospheric removal or transformation of gas-phase DDT involves photolysis, and oxidation reactions with OH,

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NO₃, or O₃ (Clifford et al., 2005). Reaction with Cl atoms may also be important in certain locations during certain times of the year (Atkinson and Arey, 2007; Nozière et al., 1999)

The most important removal reaction of DDT is initiated by reaction with OH radicals in the atmosphere. However, as the formation of OH only takes place under illumination, the OH concentration rapidly decreases after sunset. As a consequence, OH-initiated reactions only occur during the day and strongly depend on the photon flux. NO₃ undergoes rapid photolysis upon absorption of radiation. The daytime concentration of NO₃ is very low. Therefore, daytime NO₃ chemistry is expected to be unimportant for DDT. However, NO₃ has been identified and measured by long-path spectroscopic techniques in the nighttime atmosphere (Reddy et al., 2002). The reaction with NO₃ will dominate the loss pathway of DDT during nighttime.

Current knowledge of the NO₃-initiated atmospheric oxidation of DDT is very limited. The precise oxidation mechanism is not well known. This is partly due to the lack of efficient detection schemes for the short-lifetime intermediates. Quantum calculation is especially suitable for establishing whether a reaction pathway is feasible or not. In this article, we have carried out a theoretical study of the application of quantum calculations for the NO₃-initiated atmospheric oxidation reaction of DDT at the MPWB1K/6-311+G(3df,2p)//MPWB1K/6-31+G(d,p) level of theory. Several energetically favorable reaction pathways are discussed. The total and individual rate constants for the major reaction paths are given over the temperature range of 273–333 K and at atmospheric pressure using canonical variational transition-state (CVT) theory with the small curvature tunneling (SCT) method.

1 Computational methods

All of the electronic structure calculations were carried out with the Gaussian 03 suite of programs (Aliwell and Jones, 1998) on an SGI 2000 supercomputer. As a reasonable compromise between accuracy and computational cost, the geometries of the stationary points were fully optimized by employing the MPWB1K (Frisch et al., 2003) method with a standard 6-31+G(d,p) basis set. The harmonic vibrational frequencies were calculated at the same level. To acquire more reliable kinetic information, a more flexible basis set, 6-311+G(3df,2p), was employed to determine the energies of the various species. All the relative energies quoted and discussed in this article include zero-point energy (ZPE) corrections with unscaled frequencies obtained at the MPWB1K/6-31+G(d,p) level. Unscaled vibrational frequencies were employed for the calculation of ZPE corrections, stationary points characterization, and rate constant calculations. All the stationary points have been

identified for local minima and transition states for maximum by vibrational analysis. The minimum energy path (MEP) was obtained by the intrinsic reaction coordinate (IRC) theory (Zhao and Truhlar, 2004) to confirm that the transition state really connects to minima along the reaction path. Also, first and second energy derivatives at geometries along the MEP were obtained to calculate the curvature of the reaction path and to calculate the generalized vibrational frequencies along the reaction path.

Kinetic calculations were performed by using the Polyrate 9.3 program (Fukui, 1981). Canonical variational transition-state (CVT) theory (Steckler et al., 2002; Garrett and Truhlar, 1979; Baldrige et al., 1989) was applied to evaluate the theoretical rate constants. The CVT rate constant for temperature T is given by:

$$k^{\text{CVT}}(T) = \min_s k^{\text{GT}}(T, s) \quad (1)$$

$$k^{\text{GT}}(T, s) = \frac{\sigma k_{\text{B}} T}{h} \times \frac{Q^{\text{GT}}(T, s)}{\Phi^{\text{R}}(T)} e^{-V_{\text{MEP}}(s)/k_{\text{B}} T} \quad (2)$$

where, $k^{\text{GT}}(T, s)$ is the generalized transition state theory rate constant at the dividing surface s , σ is the symmetry factor accounting for the possibility of more than one symmetry-related reaction path, k_{B} is Boltzmann's constant, h is Planck's constant, $\Phi^{\text{R}}(T)$ is the reactant partition function per unit volume, excluding symmetry numbers for rotation, and $Q^{\text{GT}}(T, s)$ is the partition function of a generalized transition state at s with a local zero of energy at $V_{\text{MEP}}(s)$ and with all rotational symmetry numbers set to unity. The rotational partition functions were calculated classically, and the vibrational modes were treated as quantum-mechanically separable harmonic oscillators. In order to include quantum effects for motion along the reaction coordinate, the CVT rate constant was multiplied by a ground-state transmission coefficient. In the present work, the transmission coefficient was calculated by using the small curvature tunneling (SCT) method (Gonzalez-Lafont et al., 1991), based on the centrifugal-dominant small-curvature semi-classical adiabatic ground-state approximation.

2 Results and discussion

2.1 Reaction of DDT and NO₃

The first step of this study was to confirm the reliability of the theoretical calculations. Due to the absence of direct experimental information on the thermochemical parameters for the present reaction system, we optimized the geometries and calculated the vibrational frequencies of benzene. The geometric parameters obtained at the MPWB1K/6-31+G(d,p) level are in excellent agreement with the available experimental values. The maximum relative errors are less than 1.0% for the length of C–C

bonds and less than 0.5% for the length of C–H bonds (Fernandez-Ramos et al., 2007; Herzberg, 1996). The vibrational frequencies agree well with the experimentally observed fundamentals (Zhai and Wang, 2005), and the maximum relative error is about 6.2%.

There exist two benzene rings in the structure of DDT. Thus, NO_3 addition to the C=C double bond is a possible reaction pathway for the reaction of DDT with NO_3 radicals. In addition, as NO_3 is a strongly nucleophilic radical, H abstraction from DDT by NO_3 radicals should be another possible reaction pathway.

2.1.1 H abstraction pathways

There are two kinds of H atoms in the DDT molecule: H atoms in the alkyl group and H atoms in the benzene rings. The DDT molecule has C_s symmetry and the two

benzene rings are equivalent. Thus, only the H atoms in one benzene ring were studied. Therefore, five primary processes were identified: H abstraction from the C–H₁, C₂–H₂, C₃–H₃, C₅–H₄ and C₆–H₅ bonds. Five transition states, TS1, TS2, TS3, TS4, and TS5, were located. They were identified with only one negative eigenvalue of the Hessian matrix and, therefore, one imaginary frequency.

The pathways for the H abstraction reactions of NO_3 with DDT embedded with the potential barriers ΔE (in kcal/mol) and reaction heats ΔH (kcal/mol, 0 K) are depicted in Fig. 1. The H abstraction from the C–H₁ bond has a much lower potential barrier compared with the H abstractions from the C₂–H₂, C₃–H₃, C₅–H₄ and C₆–H₅ bonds. Furthermore, the H abstraction from the C–H₁ bond is strongly exothermic, whereas the H abstractions from the C₂–H₂, C₃–H₃, C₅–H₄ and C₆–H₅ bonds are

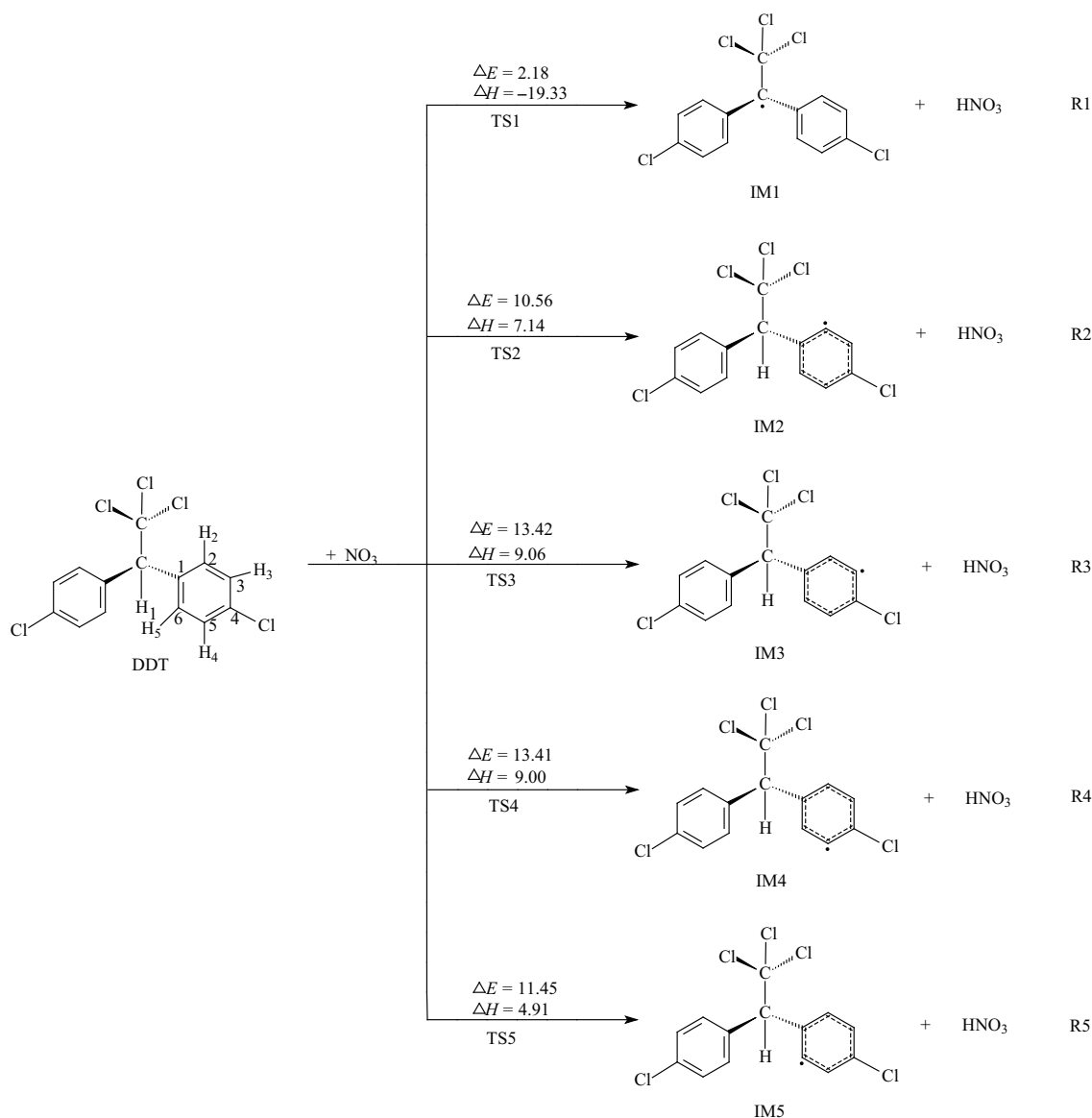


Fig. 1 Pathways for the H abstraction reactions of NO_3 with DDT. ΔE (kcal/mol): the reaction potential barrier (0 K); ΔH (kcal/mol): reaction enthalpy (0 K).

endothermic. Thus, the H abstraction from the C–H₁ bond is the thermodynamically favorable reaction pathway and can occur readily under general atmospheric conditions.

2.1.2 NO₃ addition pathways

Since the two benzene rings are equivalent in the DDT molecule, only the reaction pathways of NO₃ addition to one benzene ring were investigated. The reaction diagram can be clarified as shown in Fig. 2. Six adduct isomers, IM6, IM7, IM8, IM9, IM10 and IM11, were formed. Thus, six possible reaction pathways are found for the addition of NO₃ to the benzene ring. Calculations show that the six addition reactions are highly exothermic with low-energy barriers.

Among six pathways, pathways R8, R10 and R11 have lower potential barriers and release more heat. So path-

ways R8, R10 and R11 are the main pathways. Another three pathways are competitive.

2.2 Secondary reactions

Under atmospheric conditions, the open-shell NO₃-DDT adduct IM6-IM11 is thermally unstable, so it can rapidly react with an O₂ molecule. Figure 3 gives the pathways for the secondary reactions of NO₃-DDT adducts with O₂.

Using IM7 as an example, an O₂ molecule attacks IM7 to form an intermediate IM12, via the transition state TS12. The barrier height is 8.38 kcal/mol, and the enthalpy is –4.78 kcal/mol. A possible decomposition will occur for IM12, through a five-membered ring transition state TS13 with the barrier 14.23 kcal/mol. In this process, the O atom in the peroxy group abstracts the hydrogen atom bonded to the *ortho* carbon, which is also connected to the NO₃

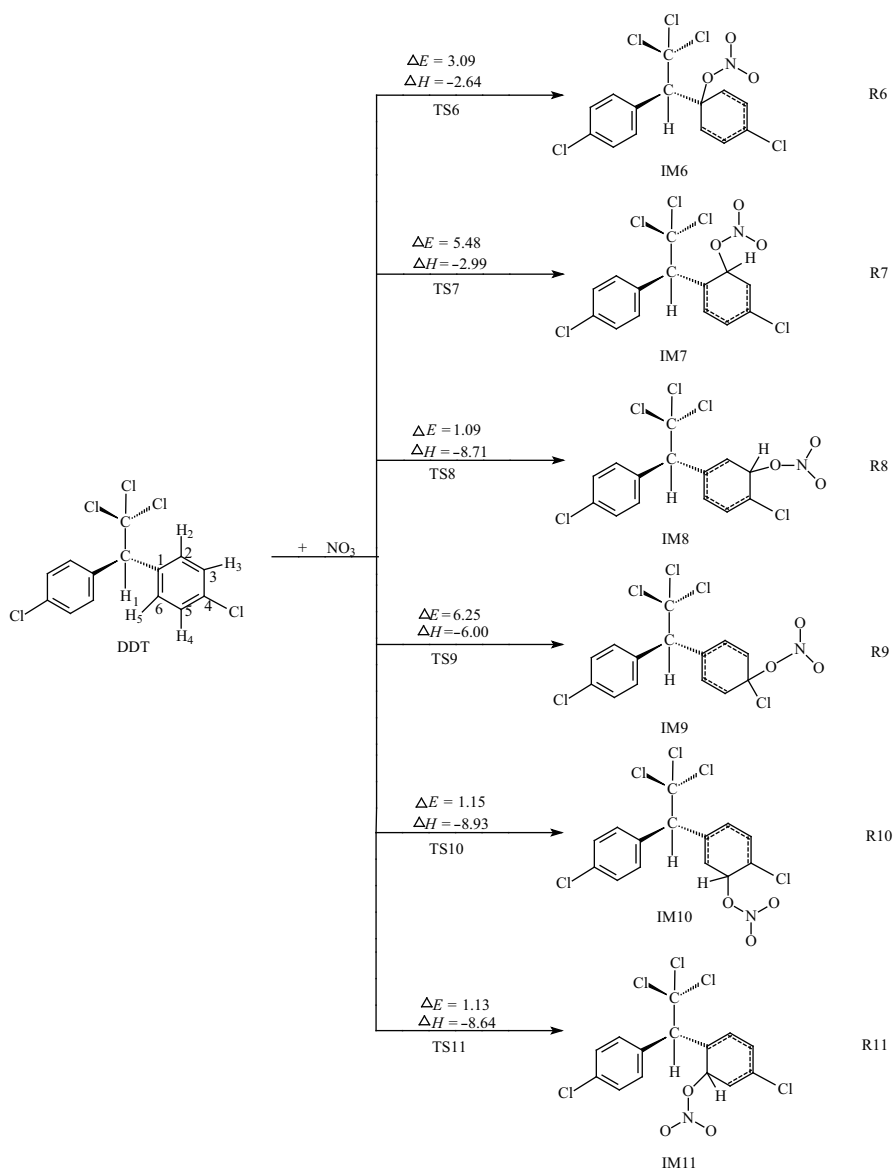


Fig. 2 Pathways for NO₃ addition reactions with DDT.

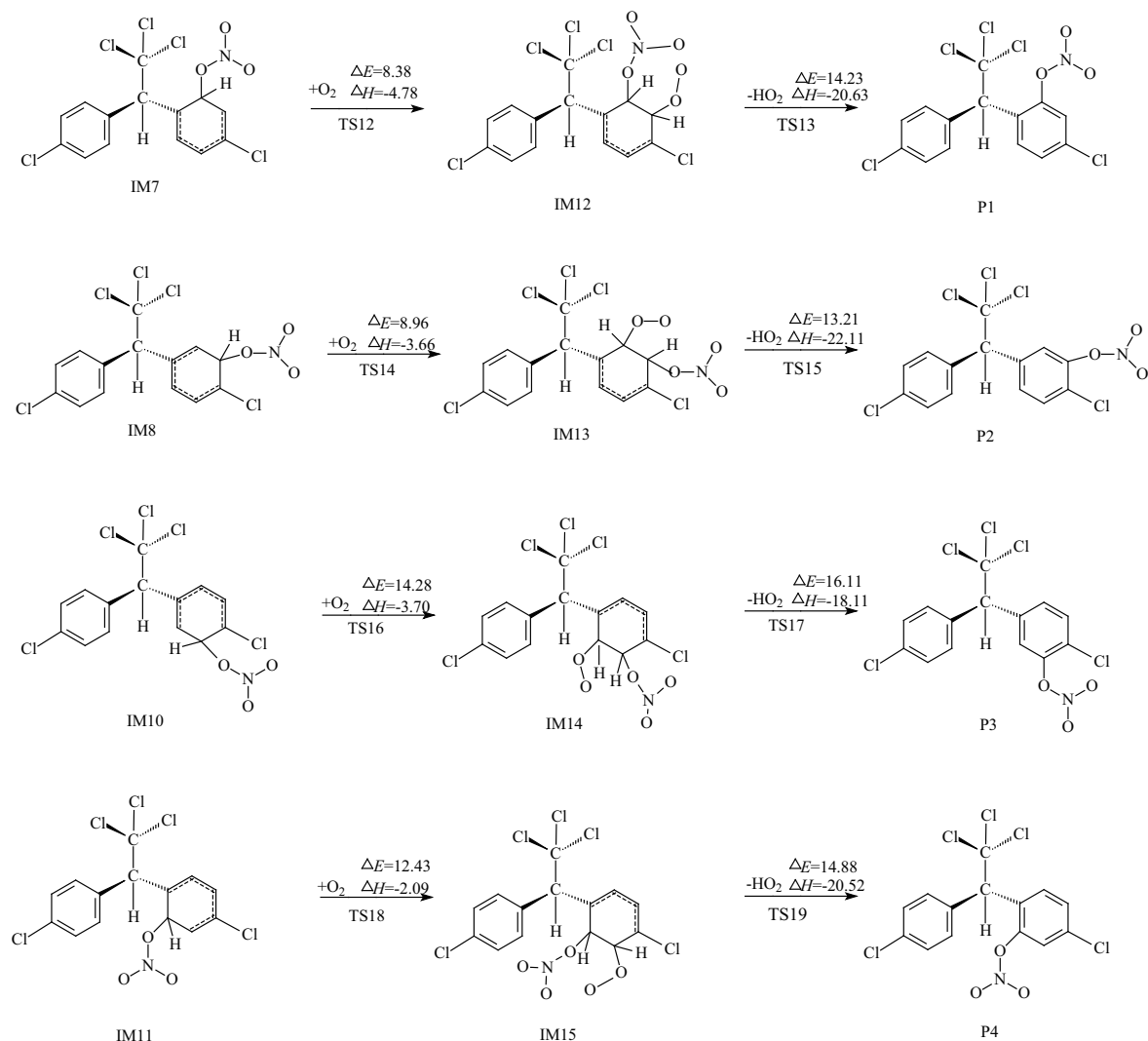


Fig. 3 Pathways for the secondary reactions of NO₃-DDT adducts with O₂.

group, and simultaneously HO₂ is produced. The product nitrate compound (P1) is obtained, as shown in Fig. 3. The one-step reaction is exothermic by 20.63 kcal/mol, and the overall reaction is strongly exothermic by 25.41 kcal/mol.

Similar to IM7, the products of IM8, IM10 and IM11 are also nitrate compounds and HO₂, as shown in Fig. 3. Data reveal that the above secondary reactions can occur readily in the atmosphere. In addition, secondary pollutant nitrate compounds have stronger carcinogenic activity and toxicity than DDT (Shimanouchi et al., Durant et al., 1996; Lewtas et al., 1990).

2.3 Rate constant calculations

The rate constants of the elementary reactions involved in the degradation of NO₃-initiated DDT were evaluated by canonical variation transition-state (CVT) theory over the temperature region of 273–333 K. The quantum tunneling effect was calculated by means of the small curvature tunneling (SCT) method, based on the centrifugal-dominant

small-curvature semiclassical adiabatic ground-state approximation. This method was used to calculate the rate constants of the initial reactions over the temperature range of 273–333 K. The calculated CVT/SCT rate constants for the NO₃ reaction with DDT are expressed in the Arrhenius form of $k = A \exp(-E_a/RT)$ (in cm³/(mol·sec)). The calculated CVT/SCT rate constants were fitted, and Arrhenius formulas are given in Table 1. The pre-exponential factor, the activation energy, and the rate constants can be obtained from these Arrhenius formulas.

From the results, we can see that the formation of IM1 from pathway R1 is faster than other H abstraction pathways and pathway R8 is the fastest formation pathway of NO₃ addition to DDT at the given temperature. Comparisons between the rate constants of pathways R1–R11 show that IM1 and IM8 are the main dynamical intermediates, and IM2–IM5 are difficult intermediates. Therefore pathways R2–R5 are not important.

For the multichannel reaction of NO₃ with DDT, the overall reaction rate constant is

Table 1 Arrhenius formulas for all reactions involved in the degradation of DDT over the temperature range of 273–333 K (unit: $\text{cm}^3/(\text{mol}\cdot\text{sec})$)

Reactions	Arrhenius equation
DDT+NO ₃ →IM1+HNO ₃	$k(T)=(2.54\times 10^{-14})\exp(-1328.53/T)$
DDT+NO ₃ →IM2+HNO ₃	$k(T)=(1.17\times 10^{-22})\exp(1526.55/T)$
DDT+NO ₃ →IM3+HNO ₃	$k(T)=(6.60\times 10^{-22})\exp(1440.48/T)$
DDT+NO ₃ →IM4+HNO ₃	$k(T)=(4.06\times 10^{-22})\exp(1532.83/T)$
DDT+NO ₃ →IM5+HNO ₃	$k(T)=(8.01\times 10^{-22})\exp(1648.81/T)$
DDT+NO ₃ →IM6	$k(T)=(5.75\times 10^{-17})\exp(-339.69/T)$
DDT+NO ₃ →IM7	$k(T)=(2.26\times 10^{-17})\exp(-305.42/T)$
DDT+NO ₃ →IM8	$k(T)=(2.00\times 10^{-15})\exp(-234.18/T)$
DDT+NO ₃ →IM9	$k(T)=(1.53\times 10^{-17})\exp(-358.01/T)$
DDT+NO ₃ →IM10	$k(T)=(6.73\times 10^{-17})\exp(-338.40/T)$
DDT+NO ₃ →IM11	$k(T)=(2.19\times 10^{-16})\exp(-513.44/T)$

denoted as k , which can be given by: $k = k_1 + 2k_2 + 2k_3 + 2k_4 + 2k_5 + 2k_6 + 2k_7 + 2k_8 + 2k_9 + 2k_{10} + 2k_{11}$. Taken together, the overall rate constant over the temperature range of 273–333 K is determined as following:

$$k(T)(\text{DDT} + \text{NO}_3) = (7.21 \times 10^{-15})\exp(-153.81/T) \quad (3)$$

At 298 K, the rate constant is $4.01 \times 10^{-15} \text{ cm}^3/(\text{mol}\cdot\text{sec})$.

The rate constant derived can be used to predict the lifetime of DDT in the atmosphere. An average NO₃ concentration is not available because of its large changes in different regions and different seasons. Therefore a medium value $1.1 \times 10^8 \text{ mol}/\text{cm}^3$ was used to calculate the atmospheric lifetime of DDT at nighttime (Stutz et al., 2004; Brown et al., 2006; Penkett et al., 2007; Allan et al., 2000; Vrekoussis et al., 2004). The atmospheric lifetime of DDT determined by NO₃ radical at nighttime can be given by:

$$\begin{aligned} \tau_{\text{NO}_3} &= \frac{1}{k \times C_{\text{NO}_3}} \\ &= \frac{1}{4.01 \times 10^{-15} \text{ cm}^3/(\text{mol}\cdot\text{sec}) \times 1.1 \times 10^8 \text{ mol}/\text{cm}^3} \quad (4) \\ &= 2.27 \times 10^6 \text{ sec}/(12 \times 3600 \text{ sec}/\text{day}) \\ &\approx 52.5 \text{ days} \end{aligned}$$

where, k is the reaction rate constant of DDT with NO₃ radical at 298 K. C_{NO_3} is the global average concentration of NO₃ radical. The half-life of 52.5 days indicates that DDT is degraded in the atmosphere very slowly and may contribute to the formation of toxic secondary organic pollutants.

3 Conclusions

In the present study, a DFT method is employed to investigate the reaction mechanism of NO₃ radical-initiated atmospheric oxidation of DDT. The rate constants were calculated by using the CVT/SCT method. Several specific conclusions can be drawn from this study. (1) For H abstraction pathways, the H atom in the alkyl is more active than the other four kinds of H atoms. (2) For addition pathways, NO₃ addition to the C₃, C₅ and C₆ atom of the benzene ring are more energetically feasible than other addition pathways. The main products of secondary reaction are nitrate compounds and HO₂. (3) The rate constants of reactions R1 and R8 are faster than those of other pathways. At 298 K, the overall rate constant is $4.01 \times 10^{-15} \text{ cm}^3/(\text{mol}\cdot\text{sec})$. The atmospheric lifetime of DDT determined by NO₃ radical is about 52.5 days, which indicates that it can be degraded in the gas phase within several months. Carcinogenic activity and toxicity of the nitrate compounds are stronger than those of DDT, which is worthy of attention. The effect of temperature on the degradation of DDT was revealed in the paper. However, the effects of other factors such as illumination were not considered. Therefore, exploration of the effects of external conditions on DDT degradation will be the subject of future work. We hope the study of NO₃-initiated atmospheric degradation of DDT can provide some information to assess the impact of these species on air quality and human health.

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