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Theoretical study on the OH-initiated atmospheric reaction of 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane (DDT)

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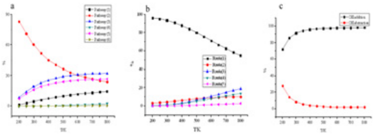
HIGHLIGHTS

- ► The OH-initiated reactions include H-abstracted and OH addition reaction.
- ► The Non-Arrhenius formulas of rate constants with the temperature are fitted.
- ► The rate constant of DDT relative to OH radical is 1.50×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

p,p′-DDT is a member of the widely used organochlorine pesticides. In this paper, the mechanism for the OH-initiated reaction of *p,p′*-DDT is studied at the MPWB1K/6–311 + G(3df,2p)//MPWB1K/6–31 + G(d,p) level. The OH addition reaction to the C_2 atom and H abstraction reaction from alkyl are energetically favorable pathways in OH-initiated reactions of DDT. On the basis of the quantum chemical information, the Rice–Ramsperger–Kassel–Marcus (RRKM) theory is used to calculate the rate constants over the temperature range of 200–800 K. The OH addition reaction is dominant according to the branching ratio, and the atmospheric lifetime of *p,p′*-DDT is 7.9 days. This work provides a comprehensive understanding of the OH-initiated atmospheric degradation of *p,p′*-DDT which is helpful for experiments and risk assessment.

1. Introduction

DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane) is one of the well known chlorine-containing pesticides, which is similar in structure to the insecticide methoxychlor and acaricide dicofol. It is reported that organochlorine pesticides residues are detected frequently both in the developed industrial countries and agricultural countries (Hong et al., 1995; Harner et al., 1999; Wu et al., 1999; Zhou et al., 2000; Kim and Smith, 2001; Manz et al., 2001). These pollutants will bring serious potential threats to human and animal health and marine ecosystem(Patlak, 1996; Tkalin, 1996; Pham et al., 1996; Hope et al., 1997; Clapp et al., 2008; Eskenazi et al., 2009; Wu et al., 2012). Most of them have the carcinogenic, teratogenic and mutagenic effect. The book entitled *Silent Spring*, published in 1962, argued that pesticides, including DDT, were poisoning both wildlife and environment and also endangering human health.

DDT is a persistent organic pollutant that is extremely hydrophobic and can be strongly absorbed in soil. Its half-life ranges from 22 days to 30 years under different conditions. There are many loss and degradation routes, for example, runoff,

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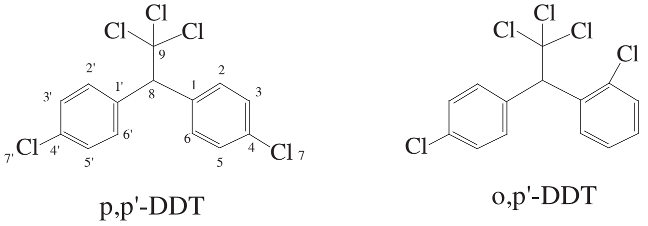
volatilization, photolysis, aerobic and anaerobic biodegradation. Many studies on the degradation of DDT in soils have been performed with different methods in recent years, such as biodegradation (Bumpus and Aust, 1987; Nadeau et al., 1994, 1998; Purnomo et al., 2008, 2010) and Fenton oxidation with zero-valent iron (Boussahel et al., 2007). But pesticides may enter the atmosphere and be transported over a long distance (Allen et al., 1998), and then the chemical reaction may play an important role in their atmospheric transport (Oehme and Ottar, 1984). The soil-to-air transfer is a big contributor to atmospheric burdens (Meijer et al., 2003). In the atmosphere, the DDT exists in the form of gas (Yao et al., 2008). The *p,p′*-DDT and its metabolites, including *p,p′*-DDE and *p,p′*-DDD are more frequently detected (Shen et al., 2005) and people are exposed to the severely toxic environment. Given the negative potential effects of what in the environment, it is crucial to study their atmospheric reactions. However, the atmospheric chemical reaction of DDT is seldom reported. The mechanism for the oxidation reactions of DDT has not been fully understood because it is difficult to detect the intermediate species in experiment. Quantum calculation is suitable to study feasible reaction pathways. The hydroxyl radical (OH) is the primary oxidant in troposphere and responsible for the removal of reactive pollutants released into the atmosphere through anthropogenic and natural processes (Seinfeld and Pandis, 1998). Thus, the study on the OH-initiated degradation of DDT is of great significance. Commercial DDT is a mixture of several closely related compounds. The major components consist of the *p,p′*-isomer and *o,p′*-isomer which account for 77% and 15%, respectively (the structure see Scheme 1). The *p,p′*-DDT, as a typical organochlorine pesticide, will be chosen to investigate the oxidative degradation in detail.

In this paper, a theoretical study on the OH-initiated atmospheric oxidative degradation of *p,p′*-DDT is carried out in order to find favorable reaction pathways. Possible subsequent reaction pathways are also researched in the presence of O_2/NO to find out the formation mechanism for secondary pollutants from the OH-initiated atmospheric reactions of the *p,p′*-DDT. The kinetic calculation is performed and the atmospheric lifetimes of reaction species are estimated.

2. Computational method

2.1. Quantum chemical calculation

The MPWB1K is an excellent method to predict transition state geometries and thermochemical kinetics, based on the modified Perdew and Wang exchange functional (MPW) and Becke's 1995 correlation functional (B95) (Zhao and Truhlar, 2004). MPWB1K method has ever been applied to study the OH-initiated oxidation reaction of organophosphorus pesticide in atmosphere (Zhou et al., 2009, 2010, 2011a,b; Bao et al., 2012). The geometry optimization and vibrational frequency calculation are performed at the MPWB1K/6–31 + G(d,p) level. The single point energy calculations are performed at the MPWB1K/6–311 + G(3df,2p) level. Each transition state calculation is verified by the intrinsic reaction coordinate (IRC) to determine certain reactants and products. All the work is performed using the Gaussian 03 programs (Frisch et al., 2003) and SGI workstation. And about the selection of functional of the computational method was detailed analysis in the supporting information.



Scheme 1. The structure of DDT (*p,p′*-DDT and *o,p′*-DDT).

2.2. Kinetic calculation

The kinetic calculations have been carried out using Rice–Ramsperger–Kassel–Marcus (RRKM) theory modified by Hou and Wang (2007). On the basis of quantum chemical calculation, the transition state theory (TST) and multichannel RRKM theory can be used to deal with atmospheric chemical reaction (Berndt and Böge, 2007; Sun et al., 2008; Zhu et al., 2009).

3. Results and discussion

3.1. OH-initiated reactions

In the atmosphere, the OH addition to the benzene ring generates a hydroxycyclohexadienyl type of radicals and the H abstraction reaction also occurs for the aromatic compounds, and the addition reaction accounts for a large proportion (Altarawneh et al., 2008). Thus, the OH radical addition reaction and the H atom abstraction reaction of *p,p′*-DDT will be discussed in this study.

Two possible reaction patterns, i.e., the OH radical addition to *p,p′*-DDT and the H atom abstraction, are calculated. Fig. 1 indicates the mechanism for the OH radical addition to *p,p′*-DDT and Fig. 2 shows the H atom abstraction reaction pattern. Fig. S1 illustrates the potential energy profile for the OH radical addition (a) and for the H atom abstraction (b). Fig. S2 shows the main geometry parameters of transition states.

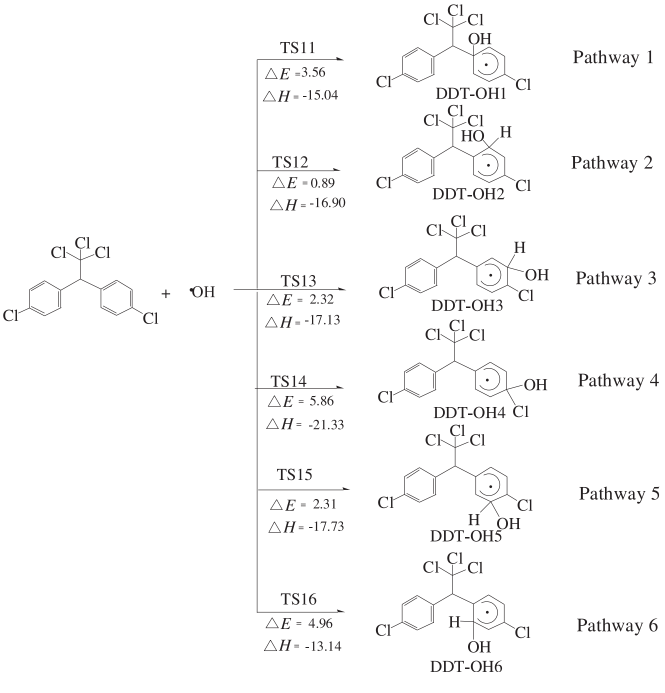


Fig. 1. The pathways of OH addition reaction with the energy barrier Δ*E* (kcal mol^{-1}) and reaction enthalpy Δ*H* (kcal mol^{-1}).