Progress and prospects of atmospheric environmental sciences in China

Fahe Chai, Abdelwahid Mellouki, Yujing Mu, Jianmin Chen, Huiwang Gao, Hong Li
CONTENTS

Special Issue: Progress and prospects of atmospheric environmental sciences in China

Preface
Fabe Chai, Abdelwahid Mellouki, Yueling Mu, Jianmin Chen, Huiwang Gao, Hong Li .................................................................................................................. 1

Haze insights and mitigation in China: An overview
Xiuliang Zhang, Yuezi Wang, Hong He, Jiaoguo Liu, Xinnong Wang, Tingyu Zhu, Manfa Ge, Zhi Zhou, Quianqian Tang, Jinzhu Ma ............................................ 2

Effectiveness of national air pollution control policies on the air quality in metropolitan areas of China
Shaxiao Wang, Jia Xing, Bin Zhao, Carey Yang, Jiming Hao .......................................................................................................................... 13

Fast increasing of surface ozone concentrations in Pearl River Delta characterized by a regional air quality monitoring network during 2006–2011
Jinfeng Li, Keding Lu, Wei Lv, Jun Li, Liujun Zhuo, Yubo Ou, Duohong Chen, Xin Huang, Yuanhang Zhang ................................................................. 23

Hygroscopicity and optical properties of alkylammonium sulfates
Dawei Hu, Chunlin Li, Hui Chen, Jianmin Chen, Xingnan Ye, Ling Li, Xin Yang, Xinnong Wang, Abdelwahid Mellouki, Zhongyang Hu ......................... 37

Photochemical properties and source of pollutants during continuous pollution episodes in Beijing, October, 2011
Jian Gao, Yuechong Zhang, Meng Zhang, Jingqiao Zhang, Shulan Wang, Jun Tao, Han Wang, Datong Luo, Fabe Chai, Chun Ren ........................................ 44

Dry deposition of PM_{10} over the Yellow Sea during Asian dust events from 2001 to 2007
Han Yan, Xiaohuan Liu, Jianhua Qi, Huiwang Gao .................................................................................................................. 54

Seasonal and diurnal variations of atmospheric peroxyacetyl nitrate, peroxypropionyl nitrate, and carbon tetrachloride in Beijing
Gen Zhang, Yuejin Mu, Junfeng Liu, Chenglong Zhang, Yuanyuan Zhang, Yue Zhang ............................................................................................ 65

Spatial and temporal variation of particulate matter and gaseous pollutants in 26 cities in China
Fabe Chai, Jian Gao, Zhenxing Chen, Shulan Wang, Yuechong Zhang, Jingqiao Zhang, Hefeng Zhang, Yan Yun, Chun Ren .................................................. 75

Wintertime peroxyacetyl nitrate (PAN) in the megacity Beijing: Role of photochemical and meteorological processes
Huolong Zhang, Xiaobin Xu, Weili Lin, Ying Wang .................................................................................................................. 83

Modeling study on seasonal variation in aerosol extinction properties over China
Yi Gao, Meigen Zhang .................................................................................. 97

Compositions and sources of organic acids in fine particles (PM_{2.5}) over the Pearl River Delta region, south China
Xiyi Zhang, Xinnong Wang, Xing Ding, Quanfu He, Zhou Zhang, Tengyu Liu, Xiaoxin Fu, Bo Gao, Yunpeng Wang, Yanli Zhang, Xueqiao Deng, Dui Wu .... 110

Carbonyl emissions from heavy-duty diesel vehicle exhaust in China and the contribution to ozone formation potential
Dong Dong, Min Shao, Yue Li, Shihua Lu, Yanjun Wang, Zhe Ji, Dagang Tang ........................................................................................................ 122

Hygroscopicity of particles generated from photooxidation of α-pinene under different oxidation conditions in the presence of sulfate seed aerosols
Biuwu Chu, Kun Wang, Hideto Takekawa, Junhua Li, Wei Zhou, Jingxun Jiang, Qinxing Ma, Hong He, Jiming Hao ............................................................... 129

Gas separation using a porous cement membrane
Weiqi Zhang, Maria Gaggl, Gregor J. G. Gluth, Frank Behrendt .................................................................................................................. 140

Characteristics of atmospheric particles and heavy metals in winter in Chang-Zhu-Tan city clusters, China
Kai Zhang, Fabe Chai, Zilong Zheng, Qing Yang, Juansheng Li, Jing Wang, Yue Zhang ........................................................................................... 147

Mechanism and rate constants for complete series reactions of 19 fluoroaromatics with atomic H
Rui Gao, Xiaoyan Sun, Wanni Yu, Qingzhu Zhang, Wenxing Wang .................................................................................................................. 154

Emission factors of polycyclic aromatic hydrocarbons from domestic coal combustion in China
Geng Chunmei, Chen Jianhua, Yang Xianyang, Ren Libong, Yin Baobui, Liu Xiaoyu, Bai Zhipeng ................................................................. 160

Oxidative capacities of size-segregated haze particles in a residential area of Beijing
Zhenquan Sun, Longyi Shao, Yuying Mu, Ying Hu .................................................................................................................. 167

Impact of emission control on regional air quality: An observational study of air pollutants before, during and after the Beijing Olympic Games
Shulan Wang, Jian Gao, Yuechong Zhang, Jingqiao Zhang, Fabe Chai, Tao Wang, Chun Ren, Wenxing Wang .............................................................. 175

Mechanism and kinetics study on the ozonolysis reaction of 2,3,7,8-TCDD in the atmosphere
Jing Bai, Xiaomin Sun, Chenxi Zhang, Chen Gong, Jinghui Hu, Jianghua Zhang ..................................................................................................... 181

Size distribution, characteristics and sources of heavy metals in haze episod in Beijing
Jingchun Duan, Jihua Tan, Jiming Hao, Fahe Chai .................................................................................................................. 189

Estimation of PM_{10} in the traffic-related atmosphere for three road types in Beijing and Guangzhou, China
Yu Wang, Jiong Li, Xiang Cheng, Xiaoxiu Liu, Dezhi Sun, Xingyu Wang ........................................................................................................ 197

Trace metals in atmospheric fine particles in one industrial urban city: Spatial variations, sources, and health implications
Shengzhen Zhou, Qi Yuan, Weijun Li, Yaling Lu, Yangmei Zhang, Wenxing Wang ..................................................................................................... 205

Pollution characteristics and health risk assessment of benzene homologues in ambient air in the northeastern urban area of Beijing, China
Lei Li, Hong Li, Xinmin Zhang, Li Wang, Linghong Xu, Xuezhong Wang, Yanting Yu, Yujie Zhang, Guan Cao ........................................................................ 214

CH_{4} emission and conversion from A/O and SBR processes in full-scale wastewater treatment plants
Yan Liu, Xiang Cheng, Xiaoxiu Liu, Dezhi Sun .................................................................................................................. 224
Mechanism and kinetics study on the ozonolysis reaction of 2,3,7,8-TCDD in the atmosphere

Jing Bai¹, Xiaomin Sun¹,*, Chenxi Zhang¹, Chen Gong¹, Jingtian Hu¹, Jianghua Zhang²

¹. Environment Research Institute, Shandong University, Jinan 250100, China
². School of Management, Shandong University, Jinan 250100, China

ARTICLE INFO

Article history:
Special issue: Progress and prospects of atmospheric environmental science in China

Keywords:
ozonolysis reaction of 2,3,7,8-TCDD
chemical mechanism and kinetics study
rate constants
atmospheric lifetime

ABSTRACT

The ozonolysis of 2,3,7,8-tetra-chlorodibenzo-p-dioxin (2,3,7,8-TCDD) is an efficient degradation way in the atmosphere. The ozonolysis process and possible reactions path of Criegee Intermediates with NO and H₂O are introduced in detail at the method of MPWB1K/6-31+G(d,p)/MPWB1K/6-311+G(3df,2p) level. In ozonolysis, H₂O is an important source of OH radical formation and initiated the subsequent degradation reaction. The Rice-Ramsperger-Kassel-Marcus (RRKM) theory was applied to calculate rate constants with the temperature ranging from 200 to 600 K. The rate constant of reaction between 2,3,7,8-TCDD and O₃ is 4.80 × 10⁻²⁰ cm³/(mole·sec) at 298 K and 760 Torr. The atmospheric lifetime of the reaction species was estimated according to rate constants, which is helpful for the atmospheric model study on the degradation and risk assessment of dioxin.

Introduction

With the increasing of environmental awareness, the persistent organic pollutants (POPs) have leaped into people’s view. As typical POPs, dioxins with the carcinogenic, teratogenic, and mutagenic effects (Schecter, 1994), are a class of structurally and chemically related polychlorinated aromatic hydrocarbons that mainly include polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzo furans (PCDFs) (Schechter et al., 2006; Kulkarni et al., 2008). PCDD/Fs are mainly emitted to the atmosphere from incineration, combustion, industrial and reservoir sources (Lin et al., 2008; Chiu et al., 2011). Chi et al. (2007, 2009) studied the historical trends of PCDD/Fs in sediments buried in a reservoir and measured atmospheric deposition by automated and traditional samplers in Northern Taiwan. Because of their biological effects and high toxicities, the investigation of dioxin’s destruction is of great significance. To destroy these recalcitrant compounds, a growing interest has been provoked in developing efficient and economically feasible remediation technologies including incineration and thermal treatment (Weber et al., 1999; Lundin and Marklund, 2005), catalytic destruction (Ide et al., 1996; Debecker et al., 2011), photocatalysis (Choi et al., 2000), photolysis (Konstantinov et al., 2000; Rayne et al., 2002; Choi et al., 2004), radiolysis (Hilarides et al., 1994), ozonolysis (Vollmuth and Niessner, 1995) and biodegradation (Mori and Kondo, 2002; Fennell et al., 2004). However, most of these methods are not suitable for the degradation of PCDD/Fs in the atmosphere. Gaseous PCDD/Fs are primarily depleted when reacting with OH, NO₃ radicals and O₃ in the atmosphere (Kwok and Atkinson, 1995; Atkinson, 1996). All of those oxidants play an important role in the atmospheric chemistry. The reaction of gaseous PCDD/Fs congener with OH is reported to be at least 8 and 3 orders of magnitude faster than their reactions with...
O}_3 and NO_3 radicals (Atkinson, 1996). And the OH and O}_3 concentration in atmosphere are 2.0 \times 10^6 \text{ mole/cm}^3 and 7.0 \times 10^{11} \text{ mole/cm}^3, respectively. Obviously the O}_3 concentration is much higher than OH radical, thus the role of ozone can not be ignored in atmospheric environment. Furthermore, the main oxidants in the atmosphere are OH radical and O}_3 during the daytime, while the main oxidants are NO}_3 and O}_3 at night. So the ozone takes effect all the time and it is a highly reactive gas with a strong oxidability, which can promote heterogeneous chemical reactions faster with the organic matters, especially those with double bonds in their chemical systems. Recently the investigation of O}_3 has aroused considerable attention (José et al., 2005; Al-Alawi et al., 2008), and many experimental and theoretical studies of the ozonolysis reactions have been carried out. Most importantly, the ozone arises from a variety of resources, including anthropogenic sources and natural sources. Given that dioxin congeners share similar chemical and physical properties, 2,3,7,8-TCDD, the most toxic congener among all dioxin congeners [Schecter et al., 2006; Kulkarni et al., 2008], is 2,3,7,8-TCDD, the most toxic congener among all dioxin congeners, which has aroused considerable attention [Schecter et al., 2006; Kulkarni et al., 2008], is 2,3,7,8-TCDD, the most toxic congener among all dioxin congeners. 2,3,7,8-TCDD [Schecter et al., 2006; Kulkarni et al., 2008].

Although the experiments of PCDD/Fs’ ozonolysis have been performed, the reaction mechanism is still not clear. Recently, ab initio molecular orbital calculation is widely adopted to interpret experimental findings and to provide theoretical understanding for chemical transformation processes. Many theoretical studies on the formation of PCDD have been reported (León et al., 2002; Khachatryan et al., 2003; Fabian and Janoschek 2006; Altarawneh et al., 2007, 2008; Zhang et al., 2008, 2010; Qu et al., 2009; Xu et al., 2010, 2011; Yu et al., 2011). Therefore, invalidation of the degradation mechanism under different conditions is necessary. Zhang et al. (2011, 2012) used quantum chemical theory to clarify the mechanism for OH-initiated degradation of 2,3,7,8-TCDD and 2,3,7,8-TCDF in the presence of O}_3 and NO/H}_2O. Wen et al. (2010) reported a possible ozonolysis degradation mechanism of the 2,3,7,8-TCDD. But it can be found that Wen’s research is only based on the stereoeffect, while the electronic effect is neglected. By means of thermodynamic and kinetic analysis, the two easiest pathways of the ozonolysis degradation over the low temperature range are given in this article. Some reactions of intermediates with NO and H}_2O are also discussed. The rate constants are calculated and the atmospheric lifetime of the reaction species is estimated accordingly.

1 Computational method

1.1 Geometry optimization

The unrestricted MPWB1K method is used to treat systems with an even number of electrons but with partial open-shell character, such as ozone, the Criegee biradicals. The MPWB1K method is a hybrid density functional theory model with excellent performance for thermochemistry, thermochemical kinetics, hydrogen bonding, and weak interactions. It is well-known that 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 the study of ozonolysis reactions (Yang et al., 2007, 2008). In all reaction channels, the geometry structures of various reactants, transition states, intermediates and products are optimized at the MPWB1K/6-311+G(d,p) level. The vibrational frequencies are also calculated at the same level to determine the nature of stationary points. The selection of basis set is important to get precise results (Zhang et al., 2000). The single-point energy calculations are performed at a higher level of theory MPWB1K/6-311+G(3df,2p). All the work is performed using the Gaussian 03 programs (Frisch et al., 2003) and SGI workstation.

1.2 Kinetic calculation

The initial information obtained from ab initio calculations allows us to calculate the rate constants. The kinetic calculations have been carried out using Rice-Ramsperger-Kassel-Marcus (RRKM) theory modified by Hou and Wang (2007). This method has been successfully used in the previous ozonolysis study (Wang et al., 2010; Sun et al., 2011).

2 Results and discussion

2.1 Ozonolysis reaction

Scheme 1 shows the structure of 2,3,7,8-TCDD. There are four different kinds of C=C double bonds labeled as A, B, C and D, respectively, which can be attacked by O}_3. According to the stereoeffect, Wen et al. (2010) has reported that the D position is the most probable pathway for 2,3,7,8-TCDD to react with O}_3. In fact, both the electronic effect and stereoeffect should be taken into consideration. The thermodynamic and kinetic calculations of the four positions with O}_3 are performed. The potential energy surface is drawn in Fig. 1. Obviously, the barriers of path A (10.29 kcal/mol) and path B (9.79 kcal/mol) are lower than those of path C (14.51 kcal/mol) and path D (14.93 kcal/mol). Due to the distinction of calculation methods, the potential barrier of path D is different from the data (12.25 kcal/mol) of Wen et al. (2010).

The ozonolysis reaction is initiated by addition of ozone to the double bonds of 2,3,7,8-TCDD to produce a primary ozonide. The unstable five-membered ring of primary ozonide can easily break up in the the C–C bond and O–O...
bonds part to generate a high-energy criegee intermediate and a relatively stable aldehyde or ketone. In this article, the four ozonolysis reactions are similar, but path A and B are chosen to discuss the mechanism since they take up the major proportion in most of the temperature range. The structures of all the reactants, intermediates, transition states and products are listed in Fig. S3.

### 2.1.1 Reaction channel A

The main possible reaction paths for the reaction of 2,3,7,8-TCDD with O3 are listed in Scheme 2. Reaction channel A is the O3 addition to the > C2 = C3 < bond. Firstly, 2,3,7,8-TCDD reacts with O3 via TSa1 to generate IMa1, with a potential barrier of 10.29 kcal/mol and the reaction heat of –36.80 kcal/mol. Then the C2–C3 and O1–O3 bonds of the five-membered ring in IMa1 will be broken via TSa2 to form IMa2, the barrier is 25.30 kcal/mol and the reaction heat is –11.00 kcal/mol. It can be seen that the IMa2 contains a benzene ring and two C=C double bonds. Obviously, the ozone can be added to the benzene ring or the C=C double bonds sequentially. With their barriers compared, the reaction IMa2 + O3 → TSa32 → IMa32 is determined to be the most probable reaction channel. The subsequent ozonolysis processes are similar to the above discussed and the whole reaction route is listed in the Scheme 1 and the profile of potential energy surface for the subsequent reactions of reaction channel A is drawn in Fig. S1.

### 2.1.2 Reaction channel B

The reaction channel B is the O3 addition to the > C1 = C2 < which has the lowest potential barrier among the four channels. Firstly, the 2,3,7,8-TCDD reacts with O3 to produce IMb1 via TSb1 with a potential barrier of 9.79 kcal/mol and a relative energy of –38.05 kcal/mol (Fig. 1). The asymmetric IMb1 is different from the symmetrical IMa1, so that the five-membered ring in IMb1 has two pathways to break and generate two intermediates, that is, IMb21 and IMb22, respectively. Similarly, IMb22 is chosen as the reactant in the subsequent reaction after

![Scheme 1 Structure of 2,3,7,8-TCDD.](image)

![Scheme 2 Main possible reaction paths for the reaction of 2,3,7,8-TCDD with O3.](image)

![Fig. 1 Profile of potential energy ∆E surface for the first step reaction of 2,3,7,8-TCDD with O3.](image)
the potential barrier and relative energy are compared (Fig. 3). The ozonolysis reaction occurs unceasingly until the products do not contain double bonds any longer. The profile of potential energy surface for the subsequent reactions of reaction channel B is drawn in Fig. S2.

The ozonolysis reaction initiated by C or D position is similar to the reaction channel A and B discussed above. Accordingly to many reported results, the unimolecular reactions such as isomerization are also very important. Consideration of the large system of reactants, the IMa2 and IMb22 are only chosen to study the mechanism of isomerization. The reaction path is described as follows:

$$\text{IMa2} \rightarrow \text{TSa3} \rightarrow \text{IMa3}$$
$$\Delta E = 40.42 \text{ kcal/mol}, \Delta H = -2.17 \text{ kcal/mol} \quad (1)$$

$$\text{IMb22} \rightarrow \text{TSb3} \rightarrow \text{IMb3}$$
$$\Delta E = 52.15 \text{ kcal/mol}, \Delta H = -46.78 \text{ kcal/mol} \quad (2)$$

From the values of reaction barrier, a conclusion can be drawn that the isomerization reactions are not easy to occur to intermediates which contain the benzene ring.

### 2.2 Reactions in the presence of NO and H₂O

It should be pointed out that the ozonolysis reactions of 2,3,7,8-TCDD discussed above will occur only on the existence of ozone. It is well known that there are many abundant atmospheric precursors in the atmosphere, such as NO and H₂O. The criegee intermediates produced from the reaction of ozonolysis of 2,3,7,8-TCDD can react easily with these precursors. Some criegee intermediates in reaction channel A and B will be chosen as research objects to discuss the reaction mechanism with NO and H₂O.

#### 2.2.1 Reaction of IMa2

In the reaction channel A, the first criegee intermediate is IMa2. The profiles of the potential energy surface of IMa2 with NO and H₂O are drawn in Fig. 4. The potential barrier and exothermic energy for the process of IMa2 + NO → S31a → IM31a + NO₂ are 9.50 kcal/mol and 78.87 kcal/mol, respectively. This low barrier energy and high exothermic energy in this process mean that the O atom abstraction by NO can occur easily. So this process is both thermodynamically and kinetically favorable. IM31a is a kind of intermediates which contains group “O=C═O” and is easy to hydrolyze.

Hasson et al. (2003) has studied the role of the water vapor in the alkene ozonolysis. It is pointed out that water vapor is an additional source of OH radicals in the reaction with criegee intermediates. The mechanism is proposed (Fig. 5) and the route R(1) is the most probable reaction channel.

IMa2 can react with H₂O to form a van der Waals complex IM3a, and then it will generate IM4a-OH via TS3a. In TS3a, the H atom of H₂O is transferred to the O atom of “C=O-O” and the OH group of H₂O approaches the C atom. The IM4a-OH will be decomposed quickly because it is a complex with rich energy. Then the OH radical will play a very important role in dioxin degradation. The energy barrier and exothermic energy of this process are 11.75 kcal/mol and 29.41 kcal/mol, respectively.
2.2.2 Reaction of IMb21 and IMb22

In the ozonolysis reaction channel B, the criegee intermediates generated from the reactions are IMb21 and IMb22. IMb21 can react with H2O which is the same as the reaction of IMa2 with H2O. The profile of the potential surface is given as follows:

\[
\text{IMb21} + \text{H}_2\text{O} \rightarrow \text{IMb3}
\]
\[
\Delta H = -9.26 \text{ kcal/mol}
\]

\[
\text{IMb3} \rightarrow \text{TSb3} \rightarrow \text{IMb4b} - \text{OH}
\]
\[
\Delta E = 5.02 \text{ kcal/mol}, \Delta H = -37.74 \text{ kcal/mol}
\]

While IMb22 can be abstracted by NO, which is similar to the reaction of IMa2 with NO.

\[
\text{IMb22} + \text{NO} \rightarrow \text{TSb2b} \rightarrow \text{IMb2b} + \text{NO}_2
\]
\[
\Delta E = 15.18 \text{ kcal/mol}, \Delta H = -75.56 \text{ kcal/mol}
\]

Here, the property of IM32b is similar to that of IM31a discussed previously. The other criegee intermediates produced in the ozonolysis reaction can also react with NO and H2O, similar to the reaction of IMa2, IMb21 and IMb22.

2.3 Rate constants and atmospheric lifetimes

So far, the whole degradation mechanism is discussed in detail. The rate constants for the reaction of PCDD/Fs with O3 have been studied by many groups. Kwok et al. (1995) has reported the rate constant for the gas-phase reaction of debenzo-p-dioxin with O3 at 297 ± 2 K and atmospheric pressure of air using a relative rate method. The rate constant is \( < 5 \times 10^{-20} \text{ cm}^3/(\text{mole-sec}) \) which is consistent with expectations based on kinetic data for gas phase reactions of O3 with other aromatic compounds.

In this study, the RRKM theory modified by Hou and Wang (2007) is used to calculate the rate constants. The generally accepted temperature ranges from –56 to 15°C in the troposphere. Flue gas temperatures of 240–260°C are generally needed for effective PCDD/Fs destruction in field tests. Then a wider range of 200–600 K is chosen to study the relationship between the temperature and rate constants.

There are no previous data for the reaction of 2,3,7,8-TCDD + O3 → TS → IM. The rate constants of each channel are listed in Table 1. The rate constants at 298.15 K are taken as examples.

\[
\text{R} + \text{O}_3 \rightarrow \text{TSa1} \rightarrow \text{IMa1}
\]
\[
k_1 = 5.66 \times 10^{-21} \text{ cm}^3/(\text{mol-sec})
\]

\[
\text{R} + \text{O}_3 \rightarrow \text{TSb1} \rightarrow \text{IMb1}
\]
\[
k_1 = 8.73 \times 10^{-21} \text{ cm}^3/(\text{mol-sec})
\]

\[
\text{R} + \text{O}_3 \rightarrow \text{TSc1} \rightarrow \text{IMc1}
\]
\[
k_1 = 3.76 \times 10^{-22} \text{ cm}^3/(\text{mol-sec})
\]

The total rate constant design formula of 2,3,7,8-TCDD with O3 is \( k_{\text{total}} = (k_1 + k_2 + k_3) \times 4 \), i.e., about \( 4.80 \times 10^{-20} \text{ cm}^3/(\text{mol-sec}) \), which is close to the experiment value \((5 \times 10^{-20} \text{ cm}^3/(\text{mol-sec}))\) of the reaction of PCDD/Fs with O3, and the difference between rate constants may be attributed to the number of Cl atoms. It seems that the RRKM rate constants are reasonable.

Apart from the height of potential barriers, the rate constants are influenced significantly by the change of

| Table 1 Rate constants of the elementary reaction of 2,3,7,8-TCDD with O3 (unit: cm^3/(mol·sec)) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| T (K) | R+O3→TSa1→IMa1 | R+O3→TSb1→IMb1 | R+O3→TSc1→IMc1 | R+O3→TSc1→IMb1 | R+O3→TSc1→IMc1 | R+O3→TSc1→IMc1 |
| 200 | 1.90E-24 | 4.77E-24 | 2.09E-26 | 5.86E-27 | 2.30E-23 |
| 250 | 2.30E-22 | 4.40E-22 | 7.59E-24 | 2.40E-24 | 2.26E-21 |
| 298.15 | 5.66E-21 | 8.73E-21 | 3.76E-22 | 1.30E-22 | 4.80E-20 |
| 300 | 6.29E-21 | 9.70E-21 | 4.32E-22 | 1.49E-22 | 5.34E-20 |
| 350 | 7.29E-20 | 9.39E-20 | 8.43E-21 | 3.11E-21 | 5.61E-19 |
| 400 | 4.90E-19 | 5.41E-19 | 8.37E-20 | 3.25E-20 | 3.54E-18 |
| 450 | 2.27E-18 | 2.20E-18 | 5.27E-19 | 2.13E-19 | 1.59E-17 |
| 500 | 8.11E-18 | 6.96E-18 | 2.40E-18 | 1.01E-18 | 5.56E-17 |
| 550 | 2.38E-17 | 1.84E-17 | 8.59E-18 | 3.72E-18 | 1.63E-16 |
| 600 | 6.00E-17 | 4.22E-17 | 2.57E-17 | 1.14E-17 | 4.14E-16 |

\( k(T) = 2.49 \times 10^{-13} \text{ exp}(-5188.93/T); \) \( k(T) = 1.00 \times 10^{-13} \text{ exp}(-4803.81/T); \) \( k(T) = 6.62 \times 10^{-13} \text{ exp}(-6286.89/T); \) \( k(T) = 3.66 \times 10^{-13} \text{ exp}(-6425.55/T); \) \( k(T) = 2.41 \times 10^{-12} \text{ exp}(-5014.17/T). \)
temperature. Evidently, the rate constants of path A and path B are larger than those of path C and path D in low temperature range. While the rate constants of path C are larger than those of path A, path B and path D in high temperature range. The branching ratios of the four paths are drawn in Fig. 6. The branching ratio of path A increase gradually with the temperature rising. The proportion of path A varies from 17% to 29% in the range of 200–600 K. The branching ratio of path B decreases gradually as the temperature rises, which takes up the largest proportion (83%) in 200 K and the smallest proportion (41%) in 600 K. The branching ratios of path C and path D increase with the temperature rising and that of path C takes the largest proportion (25%) at 600 K. It can be seen that the different paths play different roles in different degradation mechanisms.

In order to further consider the role of NO, H2O and O3 on the criegee intermediates, the rate constants of IMa2 with NO, H2O and O3 are calculated. The values are listed in the Table 2, which can provide a reference for experimental data. For the above dimolecular reaction, the reaction velocity (v) is

\[ v = k[\text{IMa2}][X] \quad X = \text{NO, H2O or O3} \]  

Since the concentration of X can be taken as a constant in the troposphere, the dimolecular reactions approximate the first order reactions. Then the roles of NO, H2O or O3 are changed vary with their concentrations in atmosphere.

The calculated rate constants for the reactions are expressed in the Arrhenius form of \( k = A \exp(-E_a/RT) \) (in \( \text{cm}^3/(\text{mole-sec}) \)). The formula is given in Tables 1 and 2.

According to the rate constants of elementary reaction, the atmospheric lifetime of the reactants can be calculated (Sun et al., 2011). The lifetimes of the 2,3,7,8-TCDD and IMa2 over the range of 200–600 K are listed in Table 3. The lifetimes of reactants are helpful in the risk assessment of hazardous materials.

The lifetime of 2,3,7,8-TCDD relative to O3 is 11.50 months at 298.15 K. The lifetimes of IMa2 relative to O3, H2O and NO are 21.05 years, 0.53 seconds and 30.09 years, respectively. Obviously, the water in atmosphere may play an important role in the degradation of IMa2.

The dioxins, including 2,3,7,8-TCDD, are distributed all over the atmosphere, such as gas phase, liquid phase, and the surface of gas-solid phase. The degradation mechanism in different phases should be further studied.

### 3 Conclusions

The ozonolysis mechanism of 2,3,7,8-TCDD is studied using the method of quantum chemistry calculation. The role of abundant precursors such as NO and H2O in the atmosphere was also discussed. The rate constants were calculated using the RRKM theory at 200–600 K and the atmospheric lifetimes are estimated. The present study leads us to draw the following conclusions: (1) There are

---

**Table 2** Rate constants of IMa2 react with O3, H2O and NO (unit: \( \text{cm}^3/(\text{mole-sec}) \))

<table>
<thead>
<tr>
<th>T (K)</th>
<th>IMa2+O3*</th>
<th>IMa2+H2O*</th>
<th>IMa2+NO*</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.94E-24</td>
<td>1.48E-19</td>
<td>7.82E-24</td>
</tr>
<tr>
<td>250</td>
<td>1.32E-22</td>
<td>1.01E-18</td>
<td>1.32E-21</td>
</tr>
<tr>
<td>298.15</td>
<td>2.15E-21</td>
<td>3.50E-18</td>
<td>3.92E-20</td>
</tr>
<tr>
<td>300</td>
<td>2.38E-21</td>
<td>3.66E-18</td>
<td>4.42E-20</td>
</tr>
<tr>
<td>350</td>
<td>1.98E-20</td>
<td>9.36E-18</td>
<td>5.83E-19</td>
</tr>
<tr>
<td>400</td>
<td>1.02E-19</td>
<td>1.93E-17</td>
<td>4.25E-18</td>
</tr>
<tr>
<td>450</td>
<td>3.08E-19</td>
<td>3.47E-17</td>
<td>2.07E-17</td>
</tr>
<tr>
<td>500</td>
<td>1.12E-18</td>
<td>5.65E-17</td>
<td>7.59E-17</td>
</tr>
<tr>
<td>550</td>
<td>2.80E-18</td>
<td>8.57E-17</td>
<td>2.25E-16</td>
</tr>
<tr>
<td>600</td>
<td>6.13E-18</td>
<td>1.23E-16</td>
<td>5.69E-16</td>
</tr>
</tbody>
</table>

* \( k(T) = 8.20 \times 10^{-15} \exp(-4480.31/T) \); \( b k(T) = 3.14 \times 10^{-15} \exp(-2010.89/T) \); \( c k(T) = 3.88 \times 10^{-12} \exp(-5440.59/T) \).

---

**Table 3** Lifetimes of 2,3,7,8-TCDD and IMa2 in atmosphere according to the rate constant at 200–600 K (unit: sec)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>2,3,7,8-TCDD</th>
<th>IMa2a</th>
<th>IMa2b</th>
<th>IMa2c</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>6.22E+10</td>
<td>7.36E+11</td>
<td>1.26E+01</td>
<td>4.76E+12</td>
</tr>
<tr>
<td>250</td>
<td>6.33E+08</td>
<td>1.08E+10</td>
<td>1.84E+00</td>
<td>2.82E+10</td>
</tr>
<tr>
<td>298.15</td>
<td>2.98E+07</td>
<td>6.64E+08</td>
<td>5.32E-01</td>
<td>9.49E+08</td>
</tr>
<tr>
<td>300</td>
<td>2.67E+07</td>
<td>6.00E+08</td>
<td>5.08E-01</td>
<td>8.42E+08</td>
</tr>
<tr>
<td>350</td>
<td>2.54E+06</td>
<td>7.22E+07</td>
<td>1.99E-01</td>
<td>6.38E+07</td>
</tr>
<tr>
<td>400</td>
<td>4.03E+05</td>
<td>1.40E+07</td>
<td>9.64E-02</td>
<td>8.76E+06</td>
</tr>
<tr>
<td>450</td>
<td>9.00E+04</td>
<td>4.64E+06</td>
<td>5.36E-02</td>
<td>1.80E+06</td>
</tr>
<tr>
<td>500</td>
<td>2.57E+04</td>
<td>1.28E+06</td>
<td>3.29E-02</td>
<td>4.90E+05</td>
</tr>
<tr>
<td>550</td>
<td>8.76E+03</td>
<td>5.10E+05</td>
<td>2.17E-02</td>
<td>1.65E+05</td>
</tr>
<tr>
<td>600</td>
<td>3.45E+03</td>
<td>2.33E+05</td>
<td>1.51E-02</td>
<td>6.54E+04</td>
</tr>
</tbody>
</table>

* O3 average concentration is about \( 7 \times 10^{11} \) mole/cm³; \( b \) water average concentration is about \( 5.375 \times 10^{17} \) mole/cm³; \( c \) NO average concentration is about \( 2.6875 \times 10^{10} \) mole/cm³.
existsence of four reaction channels, any of which can take place. The potential barriers of four intramolecular reaction sites in 2,3,7,8-TCDD with the O$_2$ show that path A and path B are lower than those of path C and path D. (2) In the ozonolysis mechanism, the water is the source of the OH radical, which can initiate the subsequent degradation. (3) The total rate constant of 2,3,7,8-TCDD with O$_2$ is 4.80 × 10$^{-20}$ cm$^3$/(mole·sec) and the lifetime is 11.50 months.

Acknowledgments

This work is supported by National Natural Science Foundation of China (No. 21277082, 21177076, 71201093), the Promotive Research Fund for Excellent Young and Middle-aged Scientists of Shandong Province (No. BS2012HZ009, BS2012SF012), the Hi-Tech Research and Development Program (863) of China (No. 2012AA06A301), the New Century Excellent Talents in University (NCET-13-0349) and the Open Project from special fund of State Key Joint Laboratory of Environment Simulation and Pollution Control (No. 13K05ESPCP).

Supporting materials

Supplementary data associated with this article can be found in the online version.

References


## Editorial Board of Journal of Environmental Sciences

### Editor-in-Chief

Hongxiao Tang  
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China

### Associate Editors-in-Chief

- Jiuhui Qu  
  Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
- Shu Tao  
  Peking University, China  
- Nigel Bell  
  Imperial College London, United Kingdom  
- Po-Keung Wong  
  The Chinese University of Hong Kong, Hong Kong, China

### Editorial Board

#### Aquatic environment

- Baoyu Gao  
  Shandong University, China  
- Maosheng Fan  
  University of Wyoming, USA  
- Chhipin Huang  
  National Chiao Tung University, Taiwan, China  
- Ng Wun Jern  
  Nanyang Environment & Water Research Institute, Singapore  
- Clark K. K. Liu  
  University of Hawaii at Manoa, USA  
- Hokyong Shon  
  University of Technology, Sydney, Australia  
- Zhiwu Wang  
  The Ohio State University, USA  
- Min Yang  
  University of Science & Technology of China  
- Michael Schloter  
  German Research Center for Environmental Health, Germany  
- Xuejun Wang  
  Peking University, China  
- Lizhong Zhu  
  Zhejiang University, China  
- Environmental toxicology and health
  - Jingwen Chen  
    Dalian University of Technology, China  
  - Junying Hu  
    Peking University, China  
  - Guibin Jiang  
    Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
  - Sijin Liu  
    Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
  - Tsuyoshi Nakanishi  
    Gifu Pharmaceutical University, Japan  
  - Willie Peijnenburg  
    University of Leiden, The Netherlands  
  - Bingsheng Zhou  
    Institute of Hydrobiology, Chinese Academy of Sciences, China  

#### Environmental catalysis and materials

- Yuesi Wang  
  Institute of Atmospheric Physics, Chinese Academy of Sciences, China  
- Yasutake Teraoka  
  Kyushu University, Japan  
- Ralph T. Yang  
  University of Michigan, USA  
- Environmental analysis and method
  - Zongwei Cai  
    Hong Kong Baptist University, Hong Kong, China  
  - Jiping Chen  
    Hong Kong Baptist University, Hong Kong, China  
  - Jianming Chen  
    Dalian University of Technology, China  
  - Min Shao  
    Peking University, China  
  - James Jay Schauer  
    University of Wisconsin-Madison, USA  
  - Minhui Yang  
    Institute of Atmospheric Physics, Chinese Academy of Sciences, China  
  - Environmental biology
    - Yong Cai  
      Institute of Hydrobiology, Chinese Academy of Sciences, China  
    - Jie-Fei Liang  
      RWTH Aachen University, Germany  
    - Henner Hollet  
      Institute of Hydrobiology, Chinese Academy of Sciences, China  
    - Lirong Song  
      Institute of Hydrobiology, Chinese Academy of Sciences, China  

#### Terrestrial environment

- Zhiping Yang  
  Beijing Normal University, China  
- Min Yang  
  University of Science & Technology of China  
- Christopher Anderson  
  Massey University, New Zealand  
- Zuoqing Cai  
  Nanjing Normal University, China  
- Xinbin Feng  
  Institute of Geochemistry, Chinese Academy of Sciences, China  
- Hongqing Hu  
  Huzhou Agricultural University, China  
- Jin-Che Lam  
  The Chinese University of Hong Kong, Hong Kong, China  
- Erwin Klimp  
  Research Centre Juelich, Agrosphere Institute, Germany  
- Peijun Li  
  Institute of Applied Ecological Engineering, Chinese Academy of Sciences, China  
- Michael Schloter  
  German Research Center for Environmental Health, Germany  
- Xuejun Wang  
  Peking University, China  
- Lizhong Zhu  
  Zhejiang University, China  
- Environmental toxicology and health
  - Jingwen Chen  
    Dalian University of Technology, China  
  - Junying Hu  
    Peking University, China  
  - Guibin Jiang  
    Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
  - Sijin Liu  
    Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China  
  - Tsuyoshi Nakanishi  
    Gifu Pharmaceutical University, Japan  
  - Willie Peijnenburg  
    University of Leiden, The Netherlands  
  - Bingsheng Zhou  
    Institute of Hydrobiology, Chinese Academy of Sciences, China  

#### Municipal solid waste and green chemistry

- Pinjing He  
  Tongji University, China  
- Environmental ecology
  - Yong Cai  
    Florida International University, USA  
  - Henner Hollet  
    RWTH Aachen University, Germany  
  - Lirong Song  
    Institute of Hydrobiology, Chinese Academy of Sciences, China  
  - Environmental biology
    - Yong Cai  
      Florida International University, USA  
    - Jie-Fei Liang  
      RWTH Aachen University, Germany  
    - Henner Hollet  
      Institute of Hydrobiology, Chinese Academy of Sciences, China  
    - Lirong Song  
      Institute of Hydrobiology, Chinese Academy of Sciences, China  

### Editorial office staff

- Managing editor  
  Qingcai Feng  
- Editors  
  Zixuan Wang, Suqin Liu, Zhengang Mao  
- English editor  
  Catherine Rice (USA)
Aims and scope

*Journal of Environmental Sciences* is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues.

The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

For subscription to electronic edition

Elsevier is responsible for subscription of the journal. Please subscribe to the journal via http://www.elsevier.com/locate/jes.

For subscription to print edition

China: Please contact the customer service, Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China. Tel: +86-10-64017032; E-mail: journal@mail.sciencep.com, or the local post office throughout China (domestic postcode: 2-580).

Outside China: Please order the journal from the Elsevier Customer Service Department at the Regional Sales Office nearest you.

Submission declaration

Submission of an article implies that the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The submission should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Submission declaration

Submission of the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The submission should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Editorial

Authors should submit manuscript online at http://www.jesc.ac.cn. In case of queries, please contact editorial office, Tel: +86-10-62920553, E-mail: jesc@263.net, jesc@rcees.ac.cn. Instruction to authors is available at http://www.jesc.ac.cn.