



Mechanistic and kinetic study on the reaction of ozone and *trans*-2-chlorovinylldichloroarsine

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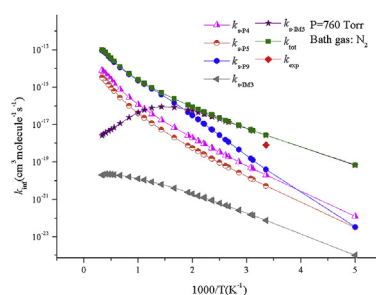
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HIGHLIGHTS

- A comprehensive mechanism of atmospheric ozonation of the lewisite are investigated theoretically.
- The results show that the As-addition/elimination is more energetically favorable than the other mechanisms.
- The rate constants for key elementary reactions were estimated by the RRKM theory.
- UV–Vis and IR spectra for important species in the lewisite + O₃ reaction are predicted.
- Products CHCl(OOO)CHAsCl₂ and CHOAsCl₂ take photolysis easily in the sunlight.

GRAPHICAL ABSTRACT



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ABSTRACT

Singlet and triplet potential energy surfaces for the atmospheric ozonation of *trans*-2-chlorovinylldichloroarsine (lewisite) are investigated theoretically. Optimizations of the reactants, products, intermediates and transition states are carried out at the BHandHLYP/6-311+G(d,p) level. Single point energy calculations are performed at the CCSD(T)/6-311+G(d,p) level based on the optimized structures. The detailed mechanism is presented and discussed. Various possible H (or Cl)-abstraction and C (or As)-addition/elimination pathways are considered. The results show that the As-addition/elimination is more energetically favorable than the other mechanisms. Rice–Ramsperger–Kassel–Marcus (RRKM) theory is used to compute the rate constants over the possible atmospheric temperature range of 200–3000 K and the pressure range of 10⁻⁸–10⁹ Torr. The calculated rate constant is in good agreement with the available experimental data. The total rate coefficient shows positive temperature dependence and pressure independence. The modified three-parameter Arrhenius expressions for the total rate coefficient and individual rate coefficients are represented. Calculation results show that major product is CHClCHAs(OOO)Cl₂ (s-IM3) at the temperature below 600 K and O₂ + CHClCHAsOCl₂ (s-

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P9) play an important role at the temperature between 600 and 3000 K. Time-dependent DFT (TD-DFT) calculations indicate that $\text{CHCl}(\text{OOO})\text{CHAsCl}_2$ (s-IM3) and CHOAsCl_2 (s-P5) can take photolysis easily in the sunlight. Due to the absence of spectral information for arsenide, computational vibrational spectra of the important intermediates and products are also analyzed to provide valuable evidence for subsequent experimental identification.

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1. Introduction

2013 Nobel Peace Prize was awarded to the Organization for the Prohibition of Chemical Weapons (OPCW) for its extensive efforts to eliminate chemical weapons. The analysis and detection of the chemical agents and their degradation products is crucially an important task in support of Chemical Weapons Convention (CWC), administered by the OPCW. During 1940 to 1945, in the former German Democratic Republic, a vast of chemical warfare agents such as diphenylchloroarsine and triphenylarsine were stored in tanks and other munitions. Then these chemical agents were poured into concrete basins (Pitten et al., 1999). As a site of Cold War heritage, Russia had 40,000 tons of chemical warfare agents stored in seven depositories. At the end of the World War II (WWII), nearly about 5300 tons of chemicals were stored in Japan and most of them were abandoned at coastal areas, buried or incinerated. It has been estimated that 674,000 chemical bombs were abandoned at the Northeast of China (Hanaoka et al., 2006). From the end of WWII, right up to the present time, the abandoned and untreated chemical warfare agents (CWAs), are being found from time to time. In recent years, further problems related to chemical weapons abandoned have been raised at many areas in the world. They represent a growing environmental and social problem in certain areas of China (You et al., 2014), Japan (Hanaoka et al., 2005, 2006; Tu, 2010) and many other countries (Pitten et al., 1999; Sanderson et al., 2014). Old CWAs munitions continue to contaminate soil, water and atmosphere besides to harm human health till today. Toxic gas leakage accident and chemical seepage in destruction of chemical weapons can lead the hydrolysis or oxidation of the original CWAs. But the environmental impact of these degradation products has been ignored by the public. To destroy the existing stockpile of CWAs all over the world is a prime objective of OPCW. All governments in the world make a concerted effort to this task for world peace. The destruction of Russia and America's stockpile of chemical weapons work is expected to be completed in 2020 and 2023. Actually, a comprehensive investigation of the potential environmental influence is indispensable before destroying a vast of CWAs in a wide range, for it will be helpful to estimate the environmental risk of the CWAs obliteration. The determination of the chemical properties of the degradation products in the environment can aid in understanding the effect on the atmospheric environment. Also, this information can potentially lead to identifying whether the degradation products cause the further environment contamination.

Lewisite is regarded as one of the most important organic arsenic compounds of CWAs (Munro et al., 1999). It was developed as a blistering chemical warfare agent (Chauhan et al., 2008; Goldman and Dacre, 1989), during the end of WWI and was named after its inventor Captain W. Lee Lewis (Haas, 1998). Lewisite was once manufactured in the U.S., Japan, and Germany for use as a chemical weapon, acting as a vesicant (blister agent) and lung irritant (Hartmann, 2002; Bismuth et al., 2004). Lewisite is usually found as a mixture of 2-chlorovinylchloroarsine (Lewisite-1), bis-(2-chlorovinyl)chloroarsine (Lewisite-2), and tris-(2-chlorovinyl)

arsine (Lewisite-3) (McDowell et al., 1948). Lewisite-2 and Lewisite-3 are the by-products of the production process of Lewisite-1, and are less toxicological significant than Lewisite-1 because of the smaller quantities and comparatively low volatility (Richard Smith et al., 1995). Lewisite-1 can exist as a trans-isomer or a cis-isomer and it was proved that the trans-isomer is the major component (Urban and von Tersch, 1999), so we focus on the reaction involving trans-Lewisite-1 rather than other compositions of lewisite in this paper. Very few studies have been conducted to understand the environmental chemistry of lewisite. In the polluted troposphere, it is recognized that ozone is one of the key products of photochemical air pollution (Finlayson-Pitts and Pitts, 1997; Jacob, 2000; Jenkin and Clemmshaw, 2000). It is rather reactive towards some important classes of organics, especially the unsaturated alkenes, and ozone reactions with such organics can contribute to their consumption (Hellman and Hamilton, 1974; Atkinson et al., 1995; Paulson et al., 1999). Numerous studies of these reactions for a large number of organics, mainly those containing unsaturated double bonds, have been reported (Paulson et al., 1999; Pompe and Veber, 2001; Kugel and Ault, 2015; Reisi-Vanani et al., 2015; Xu and Ye, 2014; Lin et al., 2014; Dang et al., 2015; Ljubić and Sabljčić, 2002). Lewisite is an organoarsenic compound with unsaturated C–C bonds and many experimental studies of lewisite-type compounds were identified carefully (Fowler et al., 1991; Rouse et al., 1998; Sasser et al., 1999; Fiddler et al., 2000; Kehe et al., 2001; Sandi et al., 2001; Lam et al., 2002; Muir et al., 2004; Kinoshita et al., 2006; Nelson et al., 2006; Strukov et al., 2010; Okumura et al., 2015). We have reported a theoretical investigation of the reaction of lewisite with OH radical in former study (Zhang et al., 2014a). However, the degradation products of the lewisite in atmosphere are still poorly understood. For this reason, the elucidation of the reactivity of lewisite towards ozone is a substantial part of determining the effect of its metabolites on the atmosphere.

The identifications of the intermediates, transition states and products of a reaction in the atmosphere are necessary for understanding their influence on the environment. However, the extreme toxicity of lewisite makes it rather challenging to capture the important species in the reactions and further to characterize the reaction mechanism, products and lifetimes of the poisonous chemicals in the atmosphere. The knowledge of these data is of immense help to unambiguous evaluation suspected lewisite in the atmosphere. Computational methods have been proved to be an effective and safe way to describe molecular structures and predict their spectroscopic properties, especially for the highly poisonous systems (Zhang et al., 2014a).

The objective of current study is to reveal the mechanism details of lewisite reaction with ozone in atmosphere. The mechanism and kinetics of lewisite reaction with ozone can be helpful for understanding the effect of the degradation products in the reaction of Lew-I with ozone. Also our investigation provides additional support to facilitate the understanding of the UV–Vis and vibrational spectral properties of the studied chemicals. The calculations may be helpful for further experimental investigation of the title

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