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Kinetic and products study of the gas-phase reaction of Lewisite with ozone under atmospheric conditions

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ABSTRACT

The rate constant for the gas-phase reaction of O₃ and Lewisite was studied in air using the smog chamber technique. The experiments were carried out under pseudo-first-order reaction conditions with [O₃] ≪ [Lewisite]. The observed rate constant of O₃ with Lewisite was $(7.83 \pm 0.38) \times 10^{-19} \text{ cm}^3 / (\text{molecule} \cdot \text{sec})$ at $298 \pm 2 \text{ K}$. Lewisite was discussed in terms of reactivity with O₃ and its relationship with the ionization potential. Our results show that the rate constant for the gas-phase reaction of O₃ with Lewisite is in line with the trend of the rate constants of O₃ with haloalkenes.

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Introduction

2-Chloroethenylarsonous dichloride (ClCH=CHAsCl₂) was first synthesized by Lewis in 1918 and named Lewisite. It is an oily liquid that contains arsenic and smells like geraniums. Lewisite has trans and cis isomers, and only the trans isomer is a type of chemical warfare agent (CWA) that causes blistering of the skin, nose, eyes and mouth on contact. Because it is completely soluble in mustard (bis-(2-chloroethyl) sulfide, another major blister agent) and has a higher vapor pressure (0.58 mmHg) than that of mustard (0.11 mmHg) (Munro et al., 1999), it was used as a Mustard–Lewisite mixture, giving an agent with high vesicant toxicity. The environmental problems of mustard were discussed by Zuo et al. (2005) and Bartelt-Hunt et al. (2006), and it is a unique aspect of atmospheric environmental chemistry (Hao et al., 2007; Wagner and Bartram, 1999).

Lewisite was once manufactured in the US, Japan, and Germany for use as a chemical warfare agent. As a result of the disarmament of Germany and Japan following World War II and subsequent general disarmament with respect to CWAs, Lewisite was abandoned at sites in the Mediterranean Sea (Amato et al., 2006) and Baltic Sea (Henriksson et al., 1996), in Europe and at Haerbaling (Hanaoka et al., 2006) in Asia in 1945. A great many safety and environmental problems have been caused over the past sixty years from the accidental exposure of people to these stockpiles. Therefore, understanding the atmospheric oxidation of CWAs should be a fundamental requirement for assessing the effects of pollutants leaking from rusting bombshells or bomb fragments (Kim et al., 2011; Yang et al., 1992).

In this paper, we used the smog chamber technique with detection of the gas-phase components by online mass

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spectrometry, blackbody Fourier transform infrared (FTIR) spectroscopy and gas chromatography to investigate products formed from the reaction of O₃ with Lewisite. To the best of our knowledge, a detailed reaction mechanism for Lewisite based on experimental measurements, such as that developed in this paper, has not yet been reported in the literature. Such a mechanism may now be applied in chemistry transport models on local or regional scales suitable for estimating the influence of Lewisite on the atmosphere if it is released from unexploded chemical ordnance dumped in China.

1. Material and methods

The experimental system used for the present study was similar to those described previously (Wang, 2013; Wang et al., 2010, 2008, 2007). Reactions were carried out in a 6 m³ (2 m × 2 m × 1.5 m) all-Teflon smog chamber equipped with a comprehensive set of sensitive instruments for measurement of ozone, temperature, pressure and humidity. The actual surface area/volume ratio of the chamber was 3.3. Ozone was generated as a mixture with O₂ by passing oxygen through an ozone generator (OZX-200YQ, Fischer Co., Ltd., Germany). An electric fan was positioned in the chamber to ensure that the reactants would be mixed completely. Before experiments were started, the chamber volume was flushed for 12 hr with 100 cm³/min matrix air purified by passing ambient air through large sorbent cartridges containing activated carbon.

Ozone reaction rate constants were determined by monitoring O₃ decay in the presence of known concentrations of the reactants. O₃ loss paths in the chamber can be considered as follows:



Ozone reaction rate constants for Eqs. (1) and (2) are k_0 and $k_{1(\text{Lewisite})}$, respectively.

Under the experimental conditions, the concentrations of Lewisite were in all cases 27 to 120 times greater than those of O₃; hence, the observed kinetics was pseudo-first order throughout the reaction:

$$-d \ln [\text{O}_3] = k' dt \quad (3)$$

where, [O₃] is the concentration of O₃, t is the reaction time, k' is the total rate constant and $k' = k_0 + k_{1(\text{Lewisite})}$. Thus, $-\frac{d \ln [\text{O}_3]}{dt}$ (ozone decay rate) was determined at various initial concentrations of Lewisite.

1.1. Lewisite concentrations

An ozonolysis experiment in the dark chamber was carried out to determine k_0 . The total loss of ozone in the absence of co-reactants in the chamber including dilution (leaking and sampling flow) and wall loss was estimated to two-standard deviations (2σ) (Bernard et al., 2012). There was no OH radical scavenger injected into the chamber in this experiment since there were few H atoms in the structure of Lewisite to yield OH radicals. The reaction was carried out under pseudo-first-order conditions (Table 1), with initial concentration of $(1.23\text{--}9.84) \times 10^{14}$ molecule/cm³ for Lewisite, $(4.03\text{--}8.37) \times 10^{12}$ molecule/cm³ for ozone. The loss rate (k_0) of ozone in these experiments was $(8.46 \pm 0.03) \times 10^{-5} \text{ sec}^{-1}$.

A gas chromatograph (GC) (SP-3420 A, Beijing Beifen-Ruili Analytical instrument (Group). Co., Ltd., China) equipped with a flame photometer detector (FPD) was used for Lewisite quantitative analysis. Lewisite in the reaction mixtures was separated on a 2 m × 4 mm stainless steel column packed with 20% SE30 on Chromosorb P (60–80 mesh) (Beijing Beifen-Ruili Analytical instrument (Group). Co., Ltd., Beijing, China). The column temperature was kept at 423 K. The injecting port temperature and the detector temperature were 453 and 513 K, respectively. Typical gas flow rates were 40 cm³/min nitrogen (carrier gas, 99.999%), 45 cm³/min hydrogen, and 45 cm³/min air. The O₃ concentrations were monitored as a function of time by a chemiluminescence ozone analyzer (Model 8410, Monitor Labs. Co., Ltd., USA). The all-Teflon smog chamber was interfaced to an on-line volatile organic contaminant mass spectrometer (SPIMS 1000, Hexin mass spectrometry Inc., China) with a sampling flow rate of 1.0 cm³/min. This instrument was designed on the basis of the time-of-flight mass spectrometer technique.

A self-made laboratory blackbody FTIR spectrometer (see diagram in Fig. 1) was used to monitor Lewisite and the products of ozone oxidation. The apparatus consists of a HFY-300B standard area source blackbody radiant point (HFY-300B, Shanghai Institute of Technical Physics of the Chinese Academy of Science, China) and a FTIR detector (vector-22, Bruker Co., Ltd., Germany) interfaced to a 1Cr18Ni9Ti stainless steel reaction cell with diameter of

Table 1 – Initial conditions and least-square liner regression parameters for pseudo-first-order reaction rate constants.

Lewisite concentration ($\times 10^{14}$ molecule/cm ³)	Ozone concentration ($\times 10^{12}$ molecule/cm ³)	k' ($\times 10^{-4} \cdot \text{sec}^{-1}$)	R
1.23	4.43	1.51 ± 0.08	0.999
2.46	4.48	2.25 ± 0.12	0.997
2.46	3.60	2.30 ± 0.08	0.999
4.92	6.75	3.70 ± 0.16	0.996
7.38	7.04	6.50 ± 0.12	0.999
9.84	8.37	8.25 ± 0.14	0.995

k' is the total rate constant with two-standard deviation (2σ).

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