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 O_3 and Lewisite was studied in air using the smog chamber technique. The experiments were carried out under pseudo-first-order reaction conditions with $[O_3] \ll [\text{Lewisite}]$. The observed rate constant of O_3 with Lewisite was $(7.83 \pm 0.38) \times 10^{-19}$ cm^3 / (molecule·sec) at 298 ± 2 K. Lewisite was discussed in terms of reactivity with O_3 and its relationship with the ionization potential. Our results show that the rate constant for the gas-phase reaction of O_3 with Lewisite is in line with the trend of the rate constants of O_3 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 O_3 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 m^3 (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 O_2 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 cm^3/min matrix air purified by passing ambient air through large sorbent cartridges containing activated carbon.

Ozone reaction rate constants were determined by monitoring O_3 decay in the presence of known concentrations of the reactants. O_3 loss paths in the chamber can be considered as follows:

$$O_3 + wall \rightarrow loss\ of\ O_3 \tag{1}$$

$$O_3 + Lewisite \rightarrow loss\ of O_3 \tag{2}$$

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

Under the experimental conditions, the concentrations of Lewisite were in all cases 27 to 120 times greater than those of O_3; hence, the observed kinetics was pseudo-first order throughout the reaction:

$$-d\ln[O_3] = k'dt \tag{3}$$

where, $[O_3]$ is the concentration of O_3, t is the reaction time, k' is the total rate constant and $k' = k_0 + k_{1(Lewisite)}$. Thus, $-\frac{d\ln[O_3]}{dt}$ (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 (1.23–9.84) × 10^{14} molecule/cm^3 for Lewisite, (4.03–8.37) × 10^{12} molecule/cm^3 for ozone. The loss rate (k_0) of ozone in these experiments was (8.46 ± 0.03) × 10^{-5} 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 cm^3/min nitrogen (carrier gas, 99.999%), 45 cm^3/min hydrogen, and 45 cm^3/min air. The O_3 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 cm^3/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 (×10^{14} molecule/cm^3)	Ozone concentration (×10^{12} molecule/cm^3)	k' (×10^{-4}·sec^{-1})	R
1.23	4.43	1.51 ± 0.08	0.999
2.46	4.48	2.25 ± 012	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).			
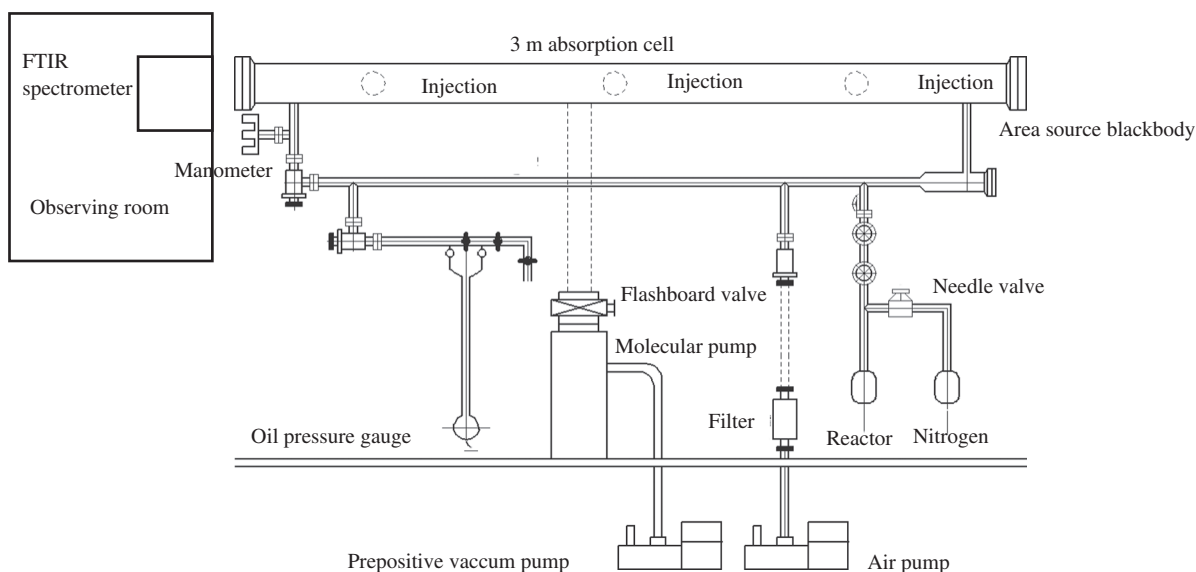
Fig. 1 – A self-made laboratory blackbody FTIR (Fourier transform infrared) spectrometer.

14.9 cm and length of 3 m. The IR entrance and exit windows of the reaction cell are made of ZnSe.

Lewisite with purity >99% was obtained from our lab (the State Key Laboratory of Nuclear Biological and Chemical Protection for Civilians, Beijing, China). Impurities can affect both the ozone decay rates and bimolecular rate constant, so a purity analysis of Lewisite must be carried out by GC before use. Because the chemical warfare agents are extremely toxic, they should be prepared and handled by trained professionals in an efficient fume hood equipped with an alkali scrubber. Individuals handling them should wear a facemask, gloves and protective suit. A decontamination solution must be kept in the workplace, and glassware and solvent waste must be properly decontaminated. N_2, O_2 and He were >99.999% (Beijing Haipu Gas Industry Company, Beijing, China); Compressed air (Beijing Huayuan Gas Industry Company, Beijing, China) was purified by passing it though silica gel, 5 A level molecular sieves and active carbon before use.

2. Results

2.1. Kinetic measurements

The plot of the ozone decay rates ($-\frac{d \ln [O_3]}{dt}$) against the Lewisite concentration is shown in Fig. 2. A good straight line was observed with the O_3 decay rates in the absence of Lewisite which is over 2 orders of magnitude less than that in the presence of Lewisite. A least-squares analysis of the data yields the bimolecular rate constant of $k_{1(Lewisite)}$ = (7.83 ± 0.38) × 10^{-19} cm^3 / (molecule·sec) at 298 ± 2 K, where the indicated error was 2 least-squares standard deviations combined with an estimated overall uncertainty of ±5.0% in the GC-FPD response factor for Lewisite. As we now know, there is no kinetic data available for the Lewisite reaction. Considering that there was no

scavenger added during the experiment, the rate constant we obtained in this study maybe an upper limit for the possibility of OH formation from the reaction between ozone and Lewisite.

According to Atkinson and Carter (1984), the rate constants for the reaction of O_3 and halogenated alkenes can be affected by the identity, number, and orientation of the substituents. In general, the electronic affects of substituents influence the rate of the addition of O_3 to halogenated alkenes, for example, an electron-withdrawing halogen substituent or a bulky steric hindrance group. Because of the strong electron-withdrawing capacity of Cl, it can reduce the charge density on the carbon atoms next to the double bond and the polarizability of the p-electrons. Compared with unsubstituted alkenes, the rate constants of halogen-substituted alkenes are low.
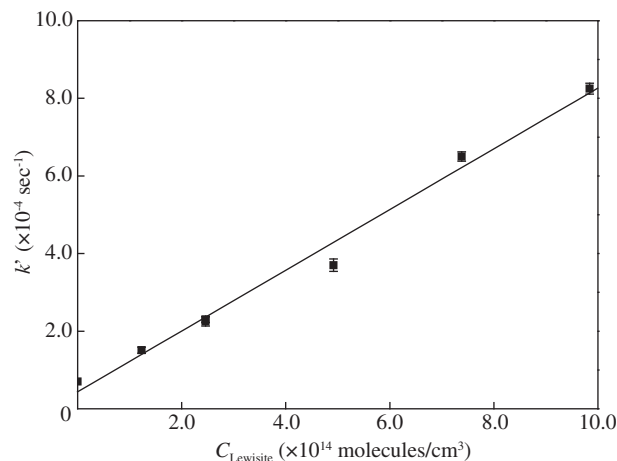

Fig. 2 – Plot of the pseudo-first-order rate constant (k') vs. concentration of Lewisite ($C_{Lewisite}$).
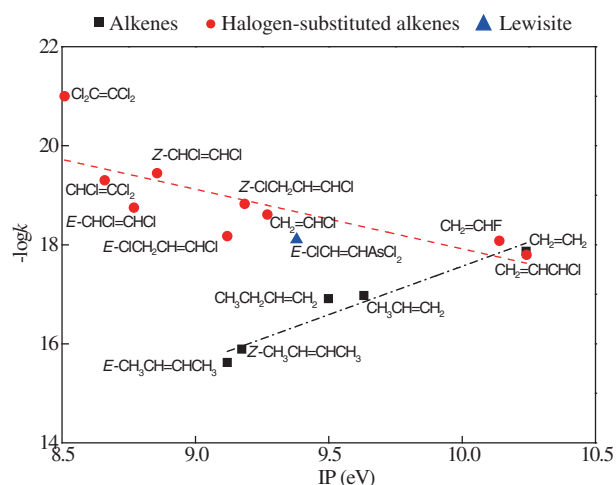
2.2. Ionization potential analysis

Two publications (Cometto et al., 2006; Lee et al., 1996) have reported that the reactivity of $O(^3P)$ atoms addition to alkenes and halogen-substituted alkenes has been found to be in line with the ionization potential (IP) of the alkenes. The above studies could be further extended to other related species such as O_3. The ionization potential is lowered in the alkenes by substitution of an H atom by an alkyl group, while the electron density of the double bond is increased by the substitution, leading to an increase in the reaction rates. By analogy to this mechanism, we listed the rate constants of O_3 with alkenes and halogen-substituted alkenes and their corresponding IP values in Table 2. Thus, it can be seen from Fig. 3 that the rate constant with O_3 increased when the IP decreased. On the other hand, it is also evident that the observed correlation between rate constant and IP did not hold for the halogenated alkenes, where the opposite trend was observed, i.e., the reaction rate constants decreased as the ionization potentials decreased. It is worth noting that the As-atom in Lewisite has a slightly metallic nature and acts as an electron-donating substituent on the double bond, producing a significant enhancement of the reactivity of the chloroethylene towards attack by the electrophilic O_3. Considering the Cl-atom is an electron-withdrawing substituent that tends to suppress the rate constant, Lewisite is less reactive than ethene ((1.35 ± 0.11) $\times 10^{-18}$ cm^3 / (molecule·sec)) (Wang et al., 2007) and more reactive than chloroethylene ((2.46 ± 0.45) $\times 10^{-19}$ cm^3 / (molecule·sec)) (Zhang et al., 1983).

Fig. 3 – $-\log k$ of O_3 reactions as a function of the ionization potential (IP) of alkenes, halogen-substituted alkenes, and Lewisite. Dashed lines serve to show a trend instead of fitting the data. k refers to the rate constants of ozone and $-\log k$ refers to negative logarithm of the rate constants of ozone.

2.3. Gas-phase product studies

Lewisite in the blackbody FTIR spectrometer reaction cell was readily observed by means of its characteristic absorption in the region 650–1000 cm^{-1} as shown in Fig. 4. The major absorption bands of trans-Lewisite included strong a C–Cl stretch absorption at 800 cm^{-1} and out-of-plane of =C–H bending vibration at 930 cm^{-1}. Product spectra of the ozone oxidation for 60 min are also shown in Fig. 4. The infrared absorption bands associated with products indicated that =C–Cl (930 cm^{-1}) groups were consumed to a great extent and C–Cl (800 cm^{-1}) groups had no evident change. The band at 730–780 cm^{-1} in Fig. 4 was assigned to the C–Cl stretch absorption of the ClCO$^-$ compound (Joo et al., 1995) based on the discussion by Atkinson and Carter (1984).

Table 2 – Experimental rate constants (k) at 298 K for the reactions of O_3 with alkenes, haloalkenes and Lewisite and their corresponding ionization potential (IP).

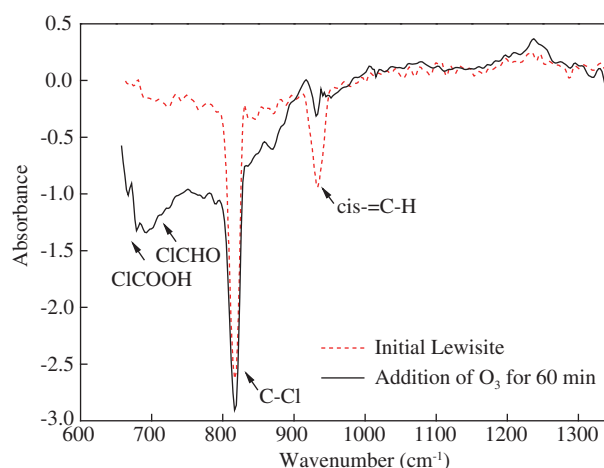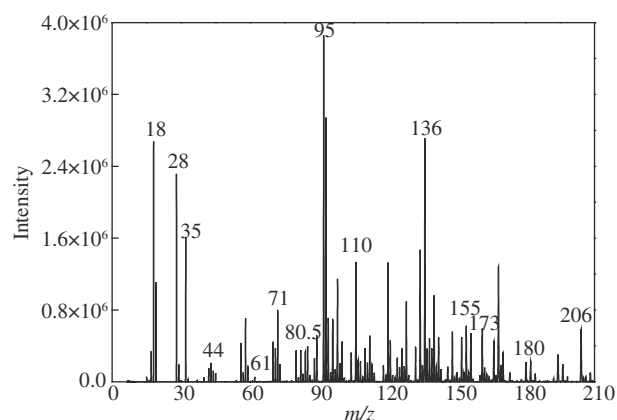| Alkene	k (10^{-19} cm^3/ (molecule·sec))	IP (eV)	Reference
$CH_2=CH_2$	13.5 ± 1.1	10.24	Wang et al. (2007)
$CH_3CH=CH_2$	106 ± 12.1	9.632	Japar et al. (1974)
$CH_3CH_2CH=CH_2$	123 ± 36.5	9.499	Japar et al. (1974)
Z-$CH_3CH=CHCH_3$	1290 ± 113	9.174	Wegener et al. (2007)
E-$CH_3CH=CHCH_3$	2380 ± 152	9.12	Wegener et al. (2007)
$CH_2=CHCH_2Cl$	16.0 ± 1.83	10.242	Tuazon et al. (1990)
$CH_2=CHF$	8.36	10.14	Adeniji et al. (1981)
E-$ClCH=CHAsCl_2$	7.83 ± 0.38	9.38	This work
$CH_2=CHCl$	2.46 ± 0.45	9.27	Zhang et al. (1983)
Z-$ClCH_2CH=CHCl$	1.5 ± 0.5	9.185	Tuazon et al. (1984)
E-$ClCH_2CH=CHCl$	6.71 ± 0.80	9.12	Tuazon et al. (1984)
Z-$CHCl=CHCl$	0.359	8.857	Zhang et al. (1983)
E-$CHCl=CHCl$	1.79 ± 0.28	8.77	Zhang et al. (1983)
$CHCl=CCl_2$	0.5	8.66	Atkinson et al., 1997
$Cl_2C=CCl_2$	0.01	8.51	Atkinson et al. (1997)

IP values are calculated in the present study using B3LYP (Becke's three-parameter hybrid functional combined with the Lee–Yang–Parr correlation functional) method.

Fig. 4 – FTIR spectra from the reaction of O_3 with Lewisite in air.

Fig. 5 – On-line time-of-flight mass spectra of the reaction O_3 with Lewisite in air.

Representative on-line time-of-flight mass spectra in the ozone oxidation experiments of Lewisite are shown in Fig. 5. The identified products from the ozone oxidation of Lewisite in the presence of air are listed in Table 3, along with their molecular structures. Ozone oxidation products can be categorized into two classes in this study, i.e., first-generation and second-generation products. The m/z 36, 61, 110, 145, 171,180 and 206 ions were observed to represent all the mass peaks of the Lewisite reactant. By comparison with the IR spectra, the m/z 80.5 and 173 ions were assigned to ClCOOH and Cl_2AsCHO as first-generation products. The m/z 18, 28, 44, 71 and 136 ions were observed to represent second-generation products. The m/z 136 ion was a possible third-generation product assigned to HCOOAsO, which came from hydrolysis of $HCOOAsCl_2$. The observed 95 m/z ion peak did not come from the products, and instead was due to volatile organic contaminants in the on-line mass spectrometer.

Based on all of the above results, the reaction of ozone with Lewisite was expected to proceed via initial addition of O_3 to the Lewisite double bond to form an energy-rich primary ozonide, which then decomposes to two carbonyl groups plus a chemically activated "Criegee" intermediate, with subsequent possible reactions as shown in Scheme 1.

The initially formed primary ozonide decomposed to yield chloride formaldehyde in path a and 2-chloroarsonous formaldehyde in path b as stable products. The initially energy-rich biradical coproducts might rearrange to a highly energetic acid and then decompose or be stabilized, or react with other species such as HCOOAsO, $AsCl_2$ and $AsOCl_2$. The $AsCl_2$ and $AsOCl_2$ would then react with H_2O in the atmosphere to yield $H_3AsO_4 \cdot 0.5H_2O$, which could be further dehydrated to As_2O_5. In the course of ozonization of Lewisite, some Cl atoms would be produced, which could react with $AsCl_2$ to form $AsCl_3$. This process was not included in the mechanism scheme because it belonged to neither path a nor path b.
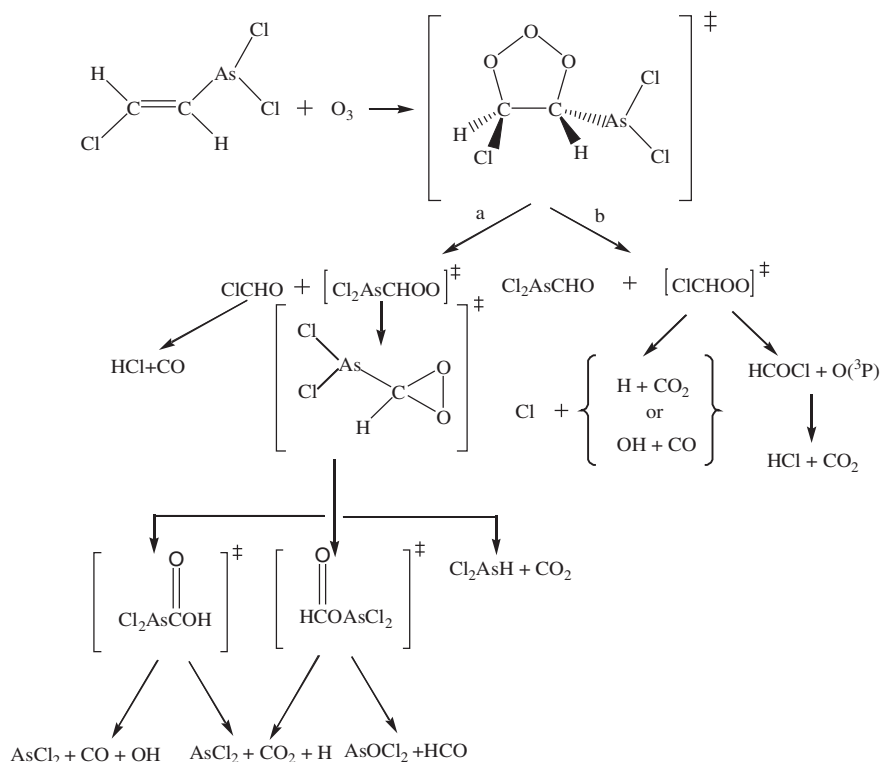
3. Discussion

The correct understanding and simulation of the tropospheric gas-phase reaction of O_3 with Lewisite are fundamental for environmental impact assessment in the process of excavating and destroying CWAs abandoned since World War II. Lewisite could be emitted into the atmosphere from unexploded chemical ordnance that has been dumped. The environmental behavior of Lewisite could be influenced by oxidation reactions with photo-oxidants in the atmosphere. As we know, the calculated atmospheric lifetimes should include the reactions with OH radical, NO_3 radical and O_3. To date, there are no experimental rate data available on the gas phase reaction of NO_3 radical with Lewisite. Recently, we obtained rate constants for the OH + Lewisite reaction using multichannel Rice–Ramsperger–Kassel–Marcus theory and transition-state theory (Zhang et al., 2014). The rate constant at 298 K and 760 mmHg for the reaction of OH with Lewisite is 1.07×10^{-15} cm^3 / (molecule·sec). Base on the relationship:

$$\tau = \frac{1}{k[OH]}$$

where, k is the rate constant of the reaction of OH with Lewisite, τ is the lifetime of Lewisite, and [OH] is the concentration of OH (2×10^6 molecule/cm^3) (Hein et al., 1997), we obtained the lifetime at 298 K and 760 Torr, i.e., $\tau_{Lewisite+OH}$ was 15 years. The gas phase reaction product of O_3 with Lewisite is considered to be an initially energy-rich biradical species. On the basis of our experimental results $(k_{1(Lewisite)} = (7.83 \pm 0.38) \times 10^{-19}$ cm^3 / (molecule·sec)), the atmospheric lifetime of Lewisite due to O_3 attack will be 15 days at 298 K at an assuming average background O_3 concentration of 1.0×10^{12} molecules/cm^3. We hypothesize that compared with the reaction of OH with Lewisite, the reaction of ozone with Lewisite constitutes a significant day-time sink, producing $H_3AsO_4 \cdot 0.5H_2O$ in the atmosphere, where $H_3AsO_4 \cdot 0.5H_2O$ is further dehydrated to As_2O_5.

Another aspect of this work is that the reaction of O_3 with alkenes and halogenated alkenes is shown to correlate with the ionization potential (IP), as observed in this experimental study. The trend of rate constants of O_3 with alkenes is completely different from that of rate constants of O_3 with halogenated alkenes. The value of the rate constant of O_3 with Lewisite from our work agrees with the trend of O_3 with haloalkenes, and therefore offers useful information for understanding the reaction process of O_3 with other halogen substituted unsaturated hydrocarbons.

Table 3 – Identified products from ozone oxidation of Lewisite.			
m/z	Product	m/z	Product
18	H_2O	95	C_2F_4
28	CO	110	AsCl
35.5	Cl	136	HCOOAsO
36.5	HCl	171	C_2H_2AsCl
44	CO_2	173	$HCOAsCl_2$
61	C_2H_2Cl	180	$AsCl_3$
71	Cl_2	206	$C_2H_2AsCl_2$
80.5	ClCOOH		

m/z refers to the ratio of mass and electric charge.

Scheme 1 – Reaction pathways of ozone with Lewisite. Paths a and b: formation of chloride formaldehyde and 2-chloroarsonous formaldehyde from primary ozonide.

4. Conclusions

The correct understanding and simulation of the tropospheric gas phase reaction of Lewisite are fundamental for use in the environmental impact assessment in the process of dealing with CWAs abandoned in China by Japan. Here, we report on our studies of the kinetics and products of the reaction of O_3 with Lewisite. Our results revealed that ozonolysis could be an important approach for Lewisite elimination compared to the other main oxidant OH in the atmosphere. In addition, the ionization potential of halogenated alkene derivatives with different substituents may be a useful parameter in further evaluation of the rate constants for the reaction of O_3 with haloalkenes.

Acknowledgments

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