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Kinetic modeling of the thermal destruction of mustard gas

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Abstract

The destruction of stockpiles or unexploded ammunitions of bis(2-chloroethyl) sulfide, also called mustard gas or yperite, by thermal treatments requires the development of highly safe processes. The high-level of toxicity of this compound induces a high level of complexity for any experiments. Consequently, there is a considerable lack of knowledge on the behavior of this chemical under high-temperature conditions (with or without oxygen). In this work a detailed chemical kinetic model for the combustion and pyrolysis of mustard gas is proposed for the first time. A large number of thermo-kinetic parameters were calculated using quantum chemistry and reaction rate theory. The model was validated against experimental pyrolysis data of the literature. It was shown that the degradation of mustard gas is ruled by a chain reaction mechanism where the chlorine atom is the principal chain carrier. HS radical, formed in the primary mechanism by an original pathway found using quantum calculations, was also proved to be an important chain carrier. Comparison with the kinetics of the usual simulant of mustard gas, diethyl sulfide, showed that the lack of chlorine atom in the former chemical leads to an inappropriate simulation of the mustard gas behavior. Combustion and pyrolysis simulations were also compared and surprisingly demonstrated that chlorine atoms remain the main chain carrier in combustion.

Keywords: Kinetic model; Toxics disposal; Quantum chemistry; Mustard gas

1. Introduction

Bis(2-chloroethyl) sulfide ($ClCH_2CH_2SCH_2CH_2Cl$), also called mustard gas, sulfur mustard, yperite or HD agent, is a vesicant chemical used as a warfare agent. This highly toxic compound has been used in many conflicts in the 20th century and has been manufactured and stored during the cold war in many countries [1–2]. Moreover, mustard

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gas has been extensively used during World War I and unexploded ammunitions are still found in western Europe [3]. The safe destruction of these stockpiles has been subject to many studies and one of the most efficient methods reported in the literature is a thermal treatment with or without oxygen [4]. Experiments with such poisonous chemicals are extremely difficult to perform.

In 2000, Battin-Leclerc et al. studied the thermal degradation of bis(2-chloroethyl) sulfide in a static reactor at a pressure of 0.16 bar for temperatures ranging between 573 and 773 K. The toxic compound was diluted in nitrogen and reaction times were varied between 1 min to 10 min. The major products measured were vinyl chloride and ethylene. A mechanistic analysis of the possible reactions was proposed by the authors. To the best of our knowledge, no detailed chemical kinetic modeling of these data has been performed in the literature. In this work, we aim to develop such a model to unravel the thermal degradation of mustard gas.

Given the toxicity of mustard gas, literature studies aiming to understand the behavior of this compound under combustion/pyrolysis conditions usually focused on simulants of bis(2-chloroethyl) sulfide. In 2009, Zheng et al. [5] studied the pyrolysis of diethyl sulfide (DES, $CH_3CH_2SCH_2CH_3$) which is assumed to be a simulant of mustard gas. Diethyl sulfide is similar to mustard gas, with the only difference residing in the replacement of the two terminal chlorine atoms by hydrogen atoms. These authors performed experiments in a flow reactor with a detailed analysis of the pyrolysis products and proposed a detailed chemical kinetic model to simulate their experiments. In 2011, the same team performed a similar study (without detailed kinetic modeling) for the pyrolysis and combustion of ethyl methyl sulfide (EMS, $CH_3SCH_2CH_3$) and observed that the conversions of EMS was significantly slower than that of DES.

In this work, we aim to develop and validate a detailed chemical kinetic model for the pyrolysis of bis(2-chloroethyl) sulfide. Extension to combustion will also be included to analyze the kinetic effects on the toxic decomposition induced by an oxidative environment. Finally, kinetic analyzes of the simulation will address the following question: is DES an appropriate simulant for the kinetics of destruction of mustard gas?

2. Chemical kinetic model development

The development of the detailed chemical model for the combustion of mustard gas was based on: a reaction basis for the combustion chemistry of C_0-C_2 compounds extended to C/H/O/S/Cl compounds featuring less than two heavy atoms, a primary mechanism including all the reactions of the target toxic, and a secondary mechanism including decomposition reactions of molecules not included in the reaction basis. More details on each of the three main parts of mechanism are listed below.

2.1. Reaction basis

The C_0-C_2 reaction basis of the EXGAS software was adopted in the model. In addition, the C_3-C_4 reaction basis featuring reactions of unsaturated hydrocarbon leading to the formation of benzene was appended [6]. The combustion reactions of C/H/O/Cl species (less than 2 heavy atoms) were taken from the work of Leylegian et al. [7] who studied the flame chemistry of CH_xCl_y compounds using experiments and kinetic modeling. The combustion reactions of sulfur species (C/H/O/S) belonging to the reaction basis were taken from the Leeds kinetic database [8].

A literature review showed that homogeneous catalytic cycles can appear for C/H/S compounds. In particular, Shum and Benson [9] proposed that during the pyrolysis of dimethyl sulfide, the addition of CH_3 onto CH_2S could lead to ethylene and HS. As no kinetic data was available for this kind of processes, we performed quantum calculations at the CBS-QB3 level of calculations to determine the potential energy surface (PES) of CH_2S+CH_3 and CH_2S+HCS. The relative energies and partition functions of the stationary points and saddle points of the PES were used to calculate the high-pressure limit rate constant and thermochemical data. Note that internal rotors were treated using the Pitzer and Gwinn approach as implemented in the ChemRate software [10]. Computed PES and associated kinetic parameters are given in Figure S1 and Table S1. Specific reactions were also added to the reaction basis for the C/H/O/S system. A set of decomposition reactions for thioformaldehyde (CH_2S) and thioacetaldehyde (CH_3CHS) was also appended, based on analogies with formaldehyde and acetaldehyde, as these compounds are formed in high concentration.

2.2. Primary mechanism

The primary mechanism includes unimolecular decompostion reactions of bis(2-chloroethyl) sulfide and all propagation reactions until a secondary molecule is formed. This molecule's decomposition reactions are either part of the reaction basis if it is small enough or will react in the secondary mechanism.

Unimolecular decomposition reactions of HD (mustard gas) involves pericyclic reactions and initial bond fissions.

The pericyclic reactions that can occur in HD decomposition are presented in reactions (1)–(3).

$$(ClCH_2CH_2)_2S \rightarrow ClCHCH_2 + ClCH_2CH_2SH \quad (1)$$