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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

1. Introduction

Bis(2-chloroethyl) sulfide ($\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$), 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 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, $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$) 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, $\text{CH}_3\text{SCH}_2\text{CH}_3$) 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 $\text{C}_0\text{-C}_2$ 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 $\text{C}_0\text{-C}_2$ reaction basis of the EXGAS software was adopted in the model. In addition, the $\text{C}_3\text{-C}_4$ 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 Unimolecular of calculations to

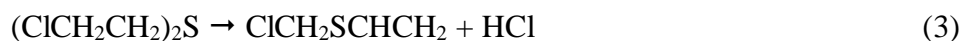
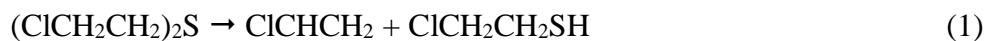
determine the potential energy surface (PES) of $\text{CH}_2\text{S}+\text{CH}_3$ and $\text{CH}_2\text{S}+\text{HCS}$. The relative energies and partition functions of the stationary points and saddle points of the PES were used to calculate the high-pressure limit rate constant and thermochemical data. 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 Sreaction basis1. 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 decomposition 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) to (3).



In reactions (1) and (2), the terminal Cl-atom (1) or H-atom (2) are transferred onto the S-atom through a 4-center cyclic transition state while the C-S bond is broken. The third pericyclic reaction (3) is a classical HCl elimination. High-pressure limit rate constants for these reactions were calculated theoretically. The kinetic parameters obtained are given in Table 1.

Table 1: High-pressure limit rate constants calculated for pericyclic decompositions in HD. Units are $\text{cm}^3, \text{mol}, \text{s}, \text{cal}$ with $k = A T^n \exp(-E/RT)$.

Reaction	A	N	E	k (s^{-1} , 1000 K)
(1)	$4.24 \cdot 10^9$	1.223	66730	$5.14 \cdot 10^{-2}$
(2)	$3.14 \cdot 10^{10}$	0.779	77640	$7.32 \cdot 10^{-5}$
(3)	$9.52 \cdot 10^{10}$	0.793	59200	2.62

Rate constants calculated at 1000 K in Table 1 show that the HCl elimination route is the most favored pericyclic pathways with a branching ratio greater than 98% for this pathway.

Initial bond fissions in HD were estimated based on bond dissociation energies computed at the CBS-QB3 level of theory. The results are given in Figure 1.

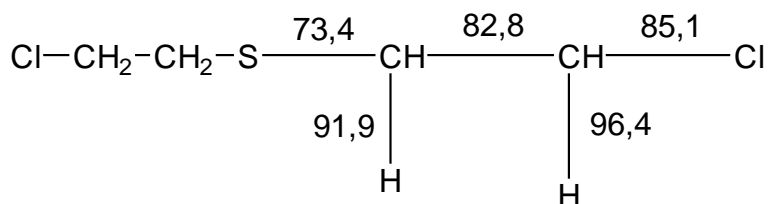


Figure 1: Bond dissociation energies in HD computed at the CBS QB3 level of theory (in kcal mol^{-1}).

From Figure 1, it can be observed that the most fragile bond in mustard gas is the C-S bond. The calculated value of $73.4 \text{ kcal mol}^{-1}$ is close to the experimental one of $73.6 \text{ kcal mol}^{-1}$ in dimethyl sulfide [11]. C-C and C-Cl bonds are the next most easiest bonds to break, respectively. C-H bonds feature high bond dissociation energies and were not included in the initial bond fission reactions.

Bimolecular initiations with O_2 were included only for the abstraction of H-atoms as the enthalpy of reaction for the abstraction of Cl are too high to play a role. Associated kinetic parameters were taken from the correlation defined in EXGAS [6]. H-abstraction reactions from HD by small radicals of the system ($\text{H}, \text{CH}_3, \text{CH}_2\text{Cl}, \text{SH}, \text{Cl}, \text{OH}, \text{O}$ and HO_2) were included in an exhaustive way. Abstractions of the chlorine atoms of HD were considered only in the reactions involving H-atoms because literature studies showed that these processes are usually kinetically negligible [7]. The high-pressure limit rate constants for the H-abstractions by H, CH_3 , CH_2Cl , and SH were computed at the

CBS-QB3 level of calculation. Kinetic parameters of the abstractions involving Cl-atoms were taken by analogies with the work of Bryukov et al. on chloroethane [12]. For the H-abstraction reactions by OH, O and HO₂, rate constants were calculated using the correlation of Dean and Bozzelli [13] based on enthalpies of reaction calculated at the CBS-QB3 level of theory. The kinetic parameters of H-abstraction reactions are given in Table S2.

Bis(2-chloroethyl) sulfide radicals, created by H-abstractions, can decompose by β -scission or internal H-transfers. Figure 2 presents the β -scission reactions included in the model in more detail.

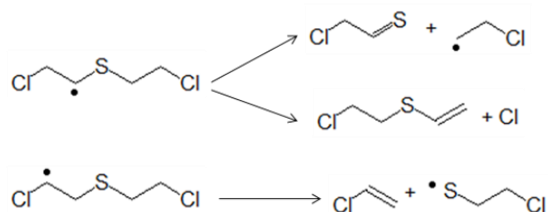


Figure 2: β -scissions of bis(2-chloroethyl) sulfide radicals

Two bis(2-chloroethyl) sulfide radicals can be produced in the radical pool. The compound with the radical center in the α -position of the S-atom can decompose by S-C bond fission, yielding chloroethyl radical and chloroethanethial, or by elimination of a chlorine atom. The other HD radical unimolecular decomposition involve the breaking of the C-S bond that lead to the formation of chlorovinyl and 2-chloroethanethiyl radical. Note that C-H β -bond fissions were neglected because of high energy barriers compared to the other pathways. Table 2 gives the high-pressure limit rate constants used in the kinetic model.

Table 2: High-pressure limit rate constants calculated for β -scission in HD radicals. Units are cm³, mol, s, cal with $k = A T^n \exp(-E/RT)$.

Réaction	A	N	E	k (s ⁻¹ , 1000 K)	Ref.
ClC ₂ H ₄ SCH(•)CH ₂ Cl=(•)CH ₂ CH ₂ Cl+ClCH ₂ CHS	8.670E+13	0.37	27685.0	9.93 10 ⁸	This work
ClC ₂ H ₄ SCH(•)CH ₂ Cl=Cl(•)+ClC ₂ H ₄ SCHCH ₂	1.660E+14	0.00	26700.0	2.42 10 ⁸	[14]
ClC ₂ H ₄ SCH ₂ CH(•)Cl=ClC ₂ H ₄ S(•)+CH ₂ CHCl	3.590E+12	0.09	9730.0	4.99 10 ¹⁰	This work

The kinetic parameters presented in Table 2 were calculated at the CBS-QB3 level of theory, except for the Cl-atom elimination which is barrierless. The high-pressure limit rate constant for the latter reaction was estimated by analogy with the experimental data of Tschuikow-Roux [14]. Note that the C-S β -bond fissions in the two HD radicals do not feature similar rate constants. The formation of chlorovinyl seems more favorable than the formation of chloroethanethial. It can be explained by a most energetically favored formation of a C=C double bond than a C=S one.

Isomerization reactions were considered only for 5- and 6-membered cyclic transition state structures. The 5-centers shift involves the transfer of a H-atom, while the 6-centers one occurs for a chlorine atom. Preliminary work showed that only the 5-center H-atom shift (connecting the two HD radicals presented in Figure 2) was the only isomerization playing a role in the primary mechanism. Therefore, the associated kinetic parameters were calculated using theoretical calculations (given in Table S2).

2.3 Secondary mechanism

The secondary mechanism (decomposition reactions of molecules not included in C/H/O/Cl/S reaction basis) was written using the same systematic decomposition reactions and reaction rate rules as the one used in the primary mechanism. This approach was adopted for molecules produced in high concentrations and important intermediates. Comprehensive decomposition reactions were included for molecular products from the successive molecular eliminations in HD and for the molecules produced by the β -scission reactions: ClCH_2CHS , $\text{ClCH}_2\text{CH}_2\text{SCHCH}_2$, $\text{ClCH}_2\text{CH}_2\text{SH}$, CH_3CHS .

3. Results and discussion

3.1 Pyrolysis of HD

The final combustion model of bis(2, chloroethyl) sulfide features 290 species and 1664 reactions. It can be obtained, in CHEMKIN format, upon request to the authors. The SENKIN code of the

CHEMKIN-II [15] program suite was used to simulate the pyrolysis data measured in a static reactor [3].

Figure 3 depicts the experimental speciation of Battin-Leclerc et al. [3], obtained for temperatures ranging between 573 and 773 K and for a pressure 0.16 bar, compared to simulations.

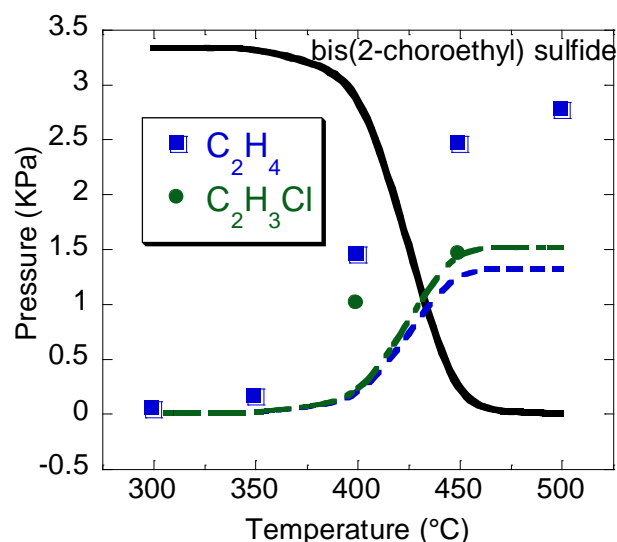


Figure 3: Evolution of partial pressures as a function of temperature during the pyrolysis of bis(2-chloroethyl) sulfide (16.67 kPa initial pressure, 10 mn residence time). Lines and symbols represent simulations and experiments [3], respectively.

A correct agreement is observed between simulations and the limited set of experimental data reported in the literature. The main experimental products detected in the Battin-Leclerc et al. experiments are ethylene and vinyl chloride as seen in Figure 3. Our model also predicts that these compounds are dominant along with HCl which was not measured by the experimentalists. These authors also reported that it was extremely difficult to follow the conversion of the reactant. They only reported that the conversion was greater than 99% at 450°C. Our simulations are in good agreement with this finding. It is interesting to note that the model predicts that CH₃CHS, H₂S, CH₂S and CH₃Cl will be produced in non negligible quantities. It is probable that unsaturated sulfur compounds will polymerize to form a yellow deposit that was reported in Zheng et al. [4] experiments.

Figure 4 presents the flux analysis performed under the experimental conditions of Battin-Leclerc et al. [3], for a limited conversion of 11%.

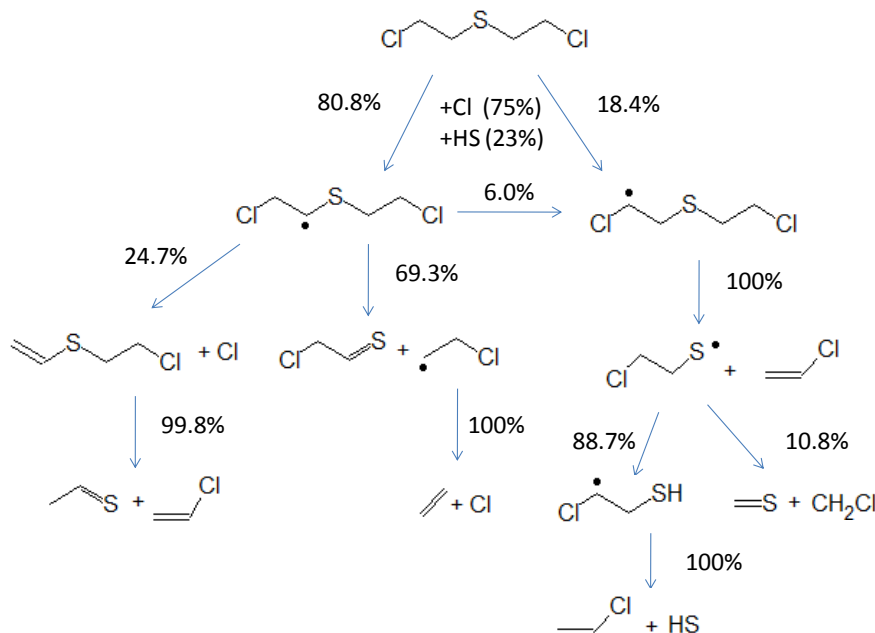


Figure 4: Reaction flux analysis for HD pyrolysis; conditions: 673 K, 0.16 bar, residence time of 10 mn corresponding to 11% of HD conversion. Given reaction fluxes (numbers associated with arrows) are relative to the consumption of a given species and are expressed in percent.

Figure 4 demonstrates that HD is initially and totally consumed by H-abstractions by Cl-atom (75%) and mercapto radical $\text{HS}\cdot$ (23%). The produced HD radicals mainly decompose by β -scission of C-S bonds. The principal consumption flux leads to the formation of $\text{ClCH}_2\text{CHS}\cdot$ and chloroethyl radical, the subsequently yields ethylene and Cl. This constitutes the dominant path of C_2H_4 formation. The second main consumption flux involves the C-S bond β -scission yielding vinylchloride and $\text{ClCH}_2\text{CH}_2\text{S}\cdot$ radical. The latter radical mainly isomerize to an intermediate $\text{ClCH}(\cdot)\text{CH}_2\text{SH}$ radical, through internal H-atom transfer, that subsequently yields vinyl chloride and HS. This flux is the only one yielding HS radical and is obviously very important as it directly impacts the global reactivity. The last main flux of consumption involves the formation of the α -radical by H-abstraction from HD, that further decomposes by C-Cl bond β -scission, leading to the formation of $\text{CH}_2\text{CHSCH}_2\text{CH}_2\text{Cl}$. This large molecule preponderantly decomposes through a retro-ene molecular elimination yielding vinylchloride

and thioacetaldehyde. Note that almost all the reactions paths highlighted in the flux diagram have been characterized using theoretical calculations.

3.2 Diethyl sulfide as a simulant of HD

Zheng et al. [5] studied the pyrolysis (experiments and detailed kinetic model) of diethyl sulfide as a, less toxic, simulant for HD behavior under thermal degradation conditions. Using the validated model for HD pyrolysis, we are now able to compare the experimental conversion of the simulant to the simulated conversion of HD. The flux analysis clearly showed that Cl-atoms was the principal chain carrier during the pyrolysis of HD. It is expected that the lack of Cl-atom in diethyl sulfide strongly affects its capacity to accurately simulate the pyrolysis behavior of HD. Figure 5 depicts the simulated conversion of HD compared to the experimental data measured for diethyl sulfide.

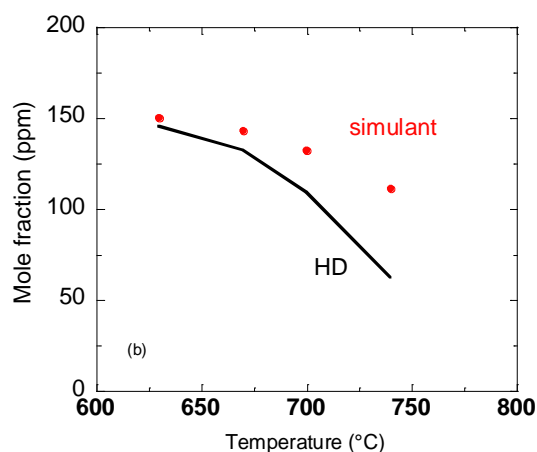


Figure 5: Comparison between experimental conversion of diethyl sulfide and simulated conversion of bis(2-chloroethyl) sulfide. Conditions taken from experiments [5]: 150 ppm of DES in N₂ in a batch reactor at atmospheric pressure with a residence time of 0.016 s.

As expected, the conversion of HD is higher than that of the simulant even at lower temperatures. The lack of chlorine atoms in the simulant explains the observed discrepancies. It is worth noting that the simulant gives a conservative estimate of the consumption of mustard gas which is a desired behaviour in the field of hazardous waste destruction. Using the chemical kinetic model of

Zheng et al. [5] to simulate the conversion of the simulant under the experimental conditions of Battin-Leclerc et al. [3] shows that the main chain carrier for this system is the H-atom. Figure S2 gives the flux analysis obtained from the model of Zheng et al. [5]. It can be noted that H-abstraction reactions from the simulant by HS radical were not included in their models as they did not find any HS formation route.

3.3 Combustion of HD

No experimental data on the combustion of mustard gas is available in the literature. However, simulations with our kinetic model will be able to compare the reactivity of HD at high-temperature, with and without oxygen. The difference in the final products distribution is also interesting from the point of view of the pollutants emitted.

Figure 6 presents the conversion of HD under combustion and pyrolysis conditions for fictive high-temperature conditions. Note that simulations were performed in an isochoric and isothermal batch reactor.

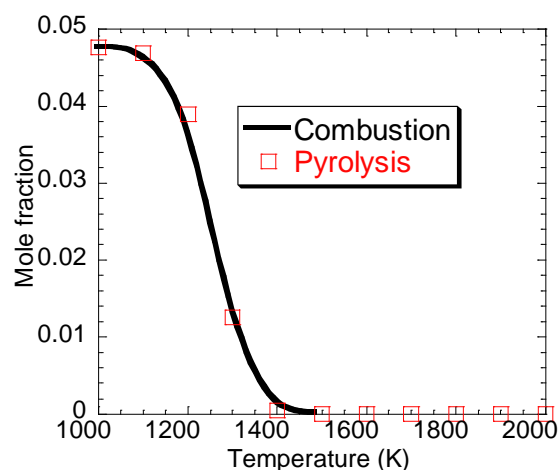


Figure 6: Simulated mole fractions of HD as a function of temperature for combustion (5% of HD in air) and pyrolysis (5% of HD in Ar) conditions (1 bar and 10 μ s residence time). Isochoric and isothermal reactor model.

Under these conditions, the conversion of HD is identical with and without oxygen. It may seem surprising, but it can be readily explained by the kinetic analysis of the modeling results. The full

reaction flux analyzes for pyrolysis and combustion under the conditions adopted in Figure 6 are given in Figure S3 of the supplemental material. It is clearly shown that even under oxidative conditions, the chlorine atom remains the main chain carrier (77 % of the total H-abstraction flux at 50% of conversion) while OH radical, the traditional preponderant chain carrier in hydrocarbon combustion, contribute to only 1% to the total H-abstraction flux. It can be also noted that under oxidative conditions, the role of HS radical (1% of the total H-abstraction flux) is lowered compared to pyrolysis (6 % of the total H-abstraction flux). This is explained by the oxidation of the sulfur compounds that slightly inhibits the reactivity of HS radical.

It can be noted that the combustion of HD in an adiabatic reactor could lead to a heat release that may eventually lead to the auto-ignition of the mixture. In this case, the reactivity would be mainly driven by the oxidation of the small species formed during the initial decomposition of the HD reactant.

The nature of the pollutant emitted during the pyrolysis or the combustion of HD is also a crucial point of safety issues for destruction processes. Figure 7 depicts the major combustion and pyrolysis products predicted by the chemical kinetic model for 100% of conversion.

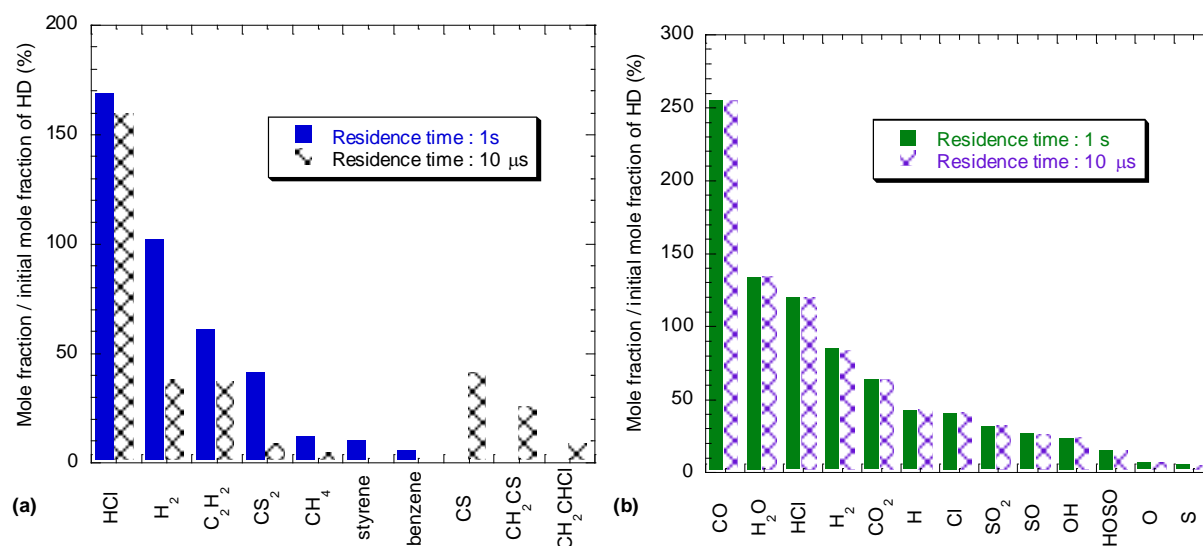


Figure 7: Pyrolysis (a) and combustion in air (b) products distribution for two residence time at 1800 K. 100% conversion of an initial HD mole fraction of 0.0476 at atmospheric pressure.

Under combustion conditions (Figure 7b), the product distribution is mostly independent of the residence time (from μs to s time scale) while pyrolysis products depends on it (Figure 7a). The most abundant combustion products are carbon monoxide and dioxide, water, hydrochloric acid, and H_2 . Several atoms and free radicals are predicted in non negligible quantities: H, Cl, SO, OH, HOSO, O and S which seem to demonstrate that the thermodynamic equilibrium is not reached under these conditions. For a residence time of 10 μs , the main pyrolysis products are HCl, H_2 , C_2H_2 , CS CH_2CS (thio ketene) and vinyl chloride. Increasing the residence time to 1s shows that the three latter compounds almost disappear while the proportion of HCl, H_2 and C_2H_2 increase and new pyrolysis products appear (CS_2 CH_4 , styrene and benzene). This can be interpreted like a classic hydrocarbon pyrolysis where intermediates are dehydrogenated and soot precursors are formed.

4. Concluding remarks

A detailed chemical kinetic model for the combustion and pyrolysis of mustard gas was developed. The primary mechanism of HD is based on a large number of quantum calculations performed at the CBS-QB3 level of theory. In particular the kinetic parameters of unimolecular decompositions, H-abstractions by H, CH_3 , CH_2Cl , and HS, β -scissions of HD radicals and internal H-transfers were determined based on theoretical calculations. The secondary mechanism was also developed following the same philosophy. A reaction basis for C/H/O/Cl/S species containing less than two heavy atoms was developed. This first kinetic model for mustard gas combustion of the literature was validated against data of the literature obtained in pyrolysis experiments. Kinetic analysis of the pyrolysis simulation showed that the pyrolysis of HD is ruled by a chain mechanism with chlorine atoms identified as the principal chain carrier. HS radical was also found to play a crucial role in the propagations. The formation route of HS was demonstrated using quantum calculations. Comparisons performed against experimental data measured for the recognized simulant of HD (diethyl sulfide) showed that this latter compound is probably not adapted to reproduce the behavior of mustard gas

under high-temperature conditions. It is explained by the lack of chlorine atoms in the molecular structure of the simulant. Under oxidative conditions, chlorine was shown to remain the dominant chain carrier despite the presence of OH radicals in the radical pool. The main pollutants predicted by the simulations for the combustion and pyrolysis of mustard gas were listed and should be a valuable input in the definition of safe destruction processes of this chemical warfare.

Acknowledgements

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