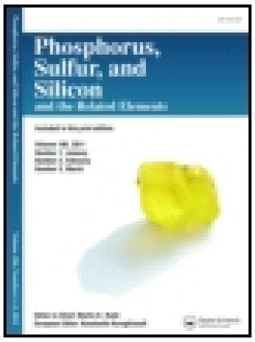

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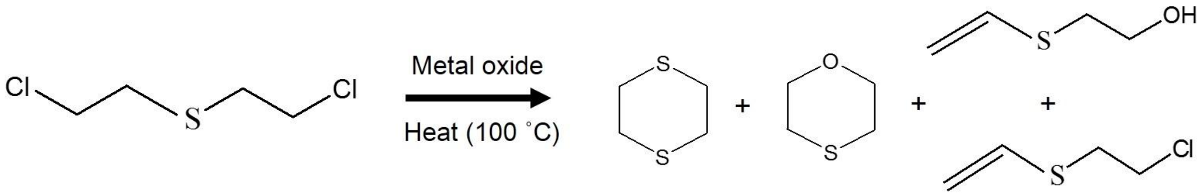
ENHANCED THERMAL DEGRADATION OF 2,2′-DICHLORODIETHYL SULFIDE (SULFUR MUSTARD, HD) WITH THE PRESENCE OF METAL OXIDES

Hyunsook Jung[*]**, Hae Wan Lee, and Eun Ah Jeong**

Agency for Defense Development, Yuseong-Gu, Daejeon 305-600, South Korea

Address correspondence to Hyunsook Jung, Agency for Defense Development, Yuseong-Gu, Daejeon 305-600, South Korea. E-mail: junghs@add.re.kr

GRAPHICAL ABSTRACT



Abstract *Thermal degradation of sulfur mustard (2,2′-dichlorodiethyl sulfide, HD) in the presence of metal oxide adsorbents was investigated by thermal desorption (TD) in conjunction with gas chromatography/mass spectrometry (GC-MS).* $Zr(OH)_4$, Al_2O_3, Al_2CoO_4, *MgO,* CeO_2, *and* V_2O_5 *were used as metal oxide adsorbents. Neat HD was spiked onto the metal oxides packed in glass tubes which were kept at room temperature and then heated at moderately elevated temperatures of 100 °C by a thermal desorption system. The products of thermal degradation were directly transferred and analyzed by GC-MS. 1,4-Dithiane and 1,4-oxathiane were characterized as the major products of the thermal degradation of HD in the presence of* $Zr(OH)_4$, Al_2O_3, Al_2CoO_4, *and* CeO_2 *adsorbents. No effective degradation was observed with MgO and* V_2O_5. *Of particular note is* $Zr(OH)_4$ *which extremely enhanced the thermal degradation of HD.*

Keywords Sulfur mustard; metal oxide; thermal degradation; 1,4-dithiane; 1,4-oxathiane

INTRODUCTION

2,2′-Dichlorodiethyl sulfide or HD (mustard gas, the common name) is one of the most well-known chemical warfare agents (CWAs). It has been used as a chemical weapon during World War I in 1917 and Iran-Iraq war in 1980s.[1, 2] Although the Chemical Weapons Convention (CWC) specified destruction of the chemical agent stockpiles and outlawed the use of mustard in 1997, it is still highly possible for terrorists or the military of rogue nations to weaponize mustard gas.[3]

HD is also a major component in stockpiles of CWAs due to its environmental stability. One effective way for destruction of HD and its related agents is incineration at high temperatures.[4] Previous work proposed that HD can be thermally degraded at high temperatures as shown in Scheme 1.[5] The major products are 1,4-dithiane and 1,2-dichloroethane which are formed via various intermediate sulfonium salts.[6] However, thermal degradation of HD in the absence of catalysis demands operating temperatures as high as 1800K at least.[4]

Metal oxides (MO_x) have been examined as effective and environmentally-friendly catalysts for the decontamination of CWAs. In particular, $Zr(OH)_4$,[7] Al_2O_3[8], CaO,[9] TiO_2[10,11] MgO[12] etc. have shown capability of degradation of HD. In general, the agent HD decomposes on the metal oxides as shown in Scheme 2.[8] The major products are chlorohydrin and thiodiglycol are formed via hydrolysis. Chloroethyl vinyl sulfide is also a major product resulting from elimination of hydrogen chloride. Although these reactions take place at room temperature, the half-lives are rather slow.[6]

Herein, we describe our experiments on the thermal degradation of HD in the presence of catalytic metal oxides. We employed a thermal desorption (TD) system in conjunction with GC-MS which directly provides heat and analyzes degraded products of HD with high selectivity and sensitivity. We also suggest a possible reaction pathway for the thermal degradation of HD in the presence of metal oxides.

RESULTS AND DISCUSSION

Following our interest in the catalytic effect of metal oxides on thermal degradation of HD, we used various metal oxide as adsorbents: $Zr(OH)_4$, Al_2O_3, Al_2CoO_4, MgO, CeO_2, and V_2O_5. Each metal oxide (~ 40 mg) was packed in a glass tube as shown in Figure 1. Then, neat HD was spiked onto the metal oxide adsorbent and the glass tube was end-capped to prevent the evaporation of neat HD. Each sample was then kept at room temperature for 6 h and then heated for 3 min at 100 °C by the thermal desorption (TD) system.

As shown in Figure 2, $Zr(OH)_4$, Al_2O_3, Al_2CoO_4, and CeO_2 effectively degraded HD. However, no effective degradation was observed in the presence of MgO and V_2O_5. It should be noted that the amount of desorbed HD was approximately equal to that of the applied HD while degraded products were merely qualitative. 1,4-Dithiane was formed as one major decomposition product with the presence of $Zr(OH)_4$ and CeO_2. Interestingly, 1,4-oxathiane was mainly detected in the presence of Al_2CoO_4, Al_2O_3, and CeO_2. In addition, vinyl species including 2-hydroxylethyl vinyl sulfide and 2-chloroethyl vinyl sulfide were formed as minor products. Unfortunately, 1,2-dichloroethane could not be detected in our experiments. Mass spectra of all products are described in Figure 3. Reportedly, 1,4-dithiane is one of the major thermal decomposition products of HD.[5] It is also known as a common degradation product of HD remaining in the environment.[13] 1,4-Dithiane is formed by dehydrochlorination via a cyclic sulfonium salt as shown in Scheme 1. However, formation of 1,4-dithiane occurs extremely slowly at ambient temperature.[14] Even at higher temperatures, the thermal degradation of HD in the absence of catalysts is known to be a slow reaction, requiring temperatures up to 1800K at least.[4] Obviously the presence of metal oxide adsorbents enhanced the thermal reactivity of HD at a relatively low temperature of 100 °C.

1,4-Oxathiane, the other major product formed in the presence of Al_2CoO_4, Al_2O_3, and CeO_2, is usually formed by dehydrochlorination of partially hydrolyzed HD (i.e., chlorohydrin as shown in Scheme 2).[8] In some cases, it may also be formed by rearrangement of 2-hydroxylethyl vinyl sulfide.[13, 17] Interestingly, chlorohydrin was not found in our study. Instead, only 2-hydroxylethyl vinyl sulfide and 2-chloroethyl vinyl sulfide were observed (see Figure 3 for their mass spectra). According to previous studies, metal oxides such as MgO and Al_2O_3 are so basic that elimination of hydrogen chloride from HD under formation of vinyl species occurs.[7, 8, 12, 18] Therefore, the basic surfaces of Al_2CoO_4, Al_2O_3, and CeO_2 enable the elimination of hydrogen chloride from HD, resulting in the elimination products 2-hydroxyethyl vinyl sulfide and 2-chloroethyl vinyl sulfide.

Of particular note is zirconium hydroxide or $Zr(OH)_4$ which extremely enhanced the thermal reactivity of HD in our study. $Zr(OH)_4$ has been reported as an effective means of removing various toxic chemicals.[7, 15, 16] It is believed that the basic hydroxyl groups of $Zr(OH)_4$ are related to its catalytic reactivity toward HD. As shown in Figure 4, 1,4-dithiane was already formed from the sample kept at room temperature for 30 min and then heated for 3 min at 100 °C. Along with 1,4-dithiane, 2-chloroethyl vinyl sulfide and 1,4-oxathiane were already formed. The time required for the complete degradation of HD was approximately 6 h. When we performed the same experiment (HD/$Zr(OH)_4$) at room temperature without heating (6 h), no effective degradation of HD was observed. Indeed, slightly detectable amounts of degraded products (i.e., 2-chloroethyl vinyl sulfide and 1,4-oxathiane) were found only as shown in Figure 5. We, therefore, attribute the extraordinary thermal reactivity of HD at the relatively low temperature of 100 °C to the catalytic effect of $Zr(OH)_4$, suggesting that thermal degradation of HD can be extremely enhanced with the presence of appropriate metal oxides even at a moderate temperature as described herein.

CONCLUSIONS

In summary, we studied thermal degradation of HD with the presence of catalytic metal oxide adsorbents. The thermal reaction of HD was effectively enhanced with $Zr(OH)_4$, Al_2O_3, Al_2CoO_4, and CeO_2. No effective degradation was observed on MgO and V_2O_5. The major products of thermal degradation of HD were 1,4-dithiane and 1,4-oxathiane, with a trace of 2-hydroxylethyl vinyl sulfide and 2-chloroethyl vinyl sulfide. Vinyl species may be formed due to alkaline metal oxide surface properties. Our results suggest that the presence of metal oxides promotes a greater extent of thermal degradation of HD, resulting in 1,4-dithiane, 1,4-oxathiane, and 2-hydroxylethyl vinyl sulfide which are known to have relatively less toxicity than HD. We hope that these results may be of value to others seeking effective methods for the mass destruction for HD and related agents.

EXPERIMENTAL

All metal oxides were obtained from Aldrich and used without further purification. The source of sulfur mustard was distilled sulfur mustard (HD), which was shown to be 98 % pure by GC and NMR. (Caution: sulfur mustard is a highly toxic vesicant chemical, and an extreme care must be taken to prevent exposure to liquid or vapor. It should only be handled by trained personnel with protective ensemble).

Neat HD (1 μL) was spiked onto the metal oxides (~ 40 mg) in glass tubes which were pre-filled with glass wool, metal oxides, and Teflon. Each sample was kept at room temperature for a certain time and then heated at 100 °C for 3 min for thermal degradation. The desorption was performed for 5 min at 250 °C using a UNITY/ULTRA thermal desorption (TD) system (Markes International, UK). The desorbed samples from each tube were then transferred to GC-MS (Agilent 7890 GC, 5973 MSD) via a heated transfer line (120 °C) at a flow rate of 20 mL/min. Separation was achieved on a 30m x 0.25mm HP-5MS GC-MS capillary column. The column oven temperature was programmed from 80 °C (kept for 3 min) to 260 °C at 15 °/min. The column flow rate was 1.2 mL/min at a constant pressure of 10.3 psi. The injection port and detector temperature were 250 °C, MSD transfer line 280 °C, MSD quad 150 °C, and MSD source 230 °C. The samples were analyzed in the electron impact (EI) mode scanning from 30-300 amu with 5.19 scans/s.

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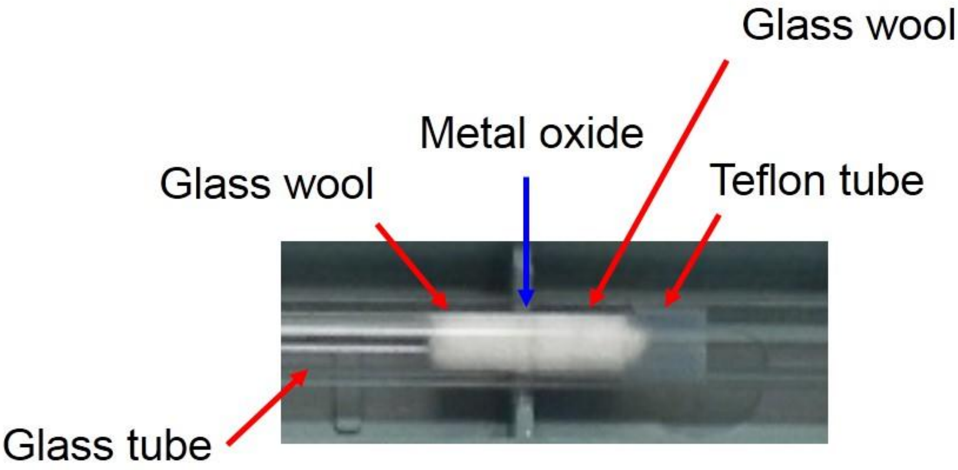


Figure 1 Representative picture of a sample constructed for thermal decomposition of HD with the presence of metal oxide adsorbent in a glass tube

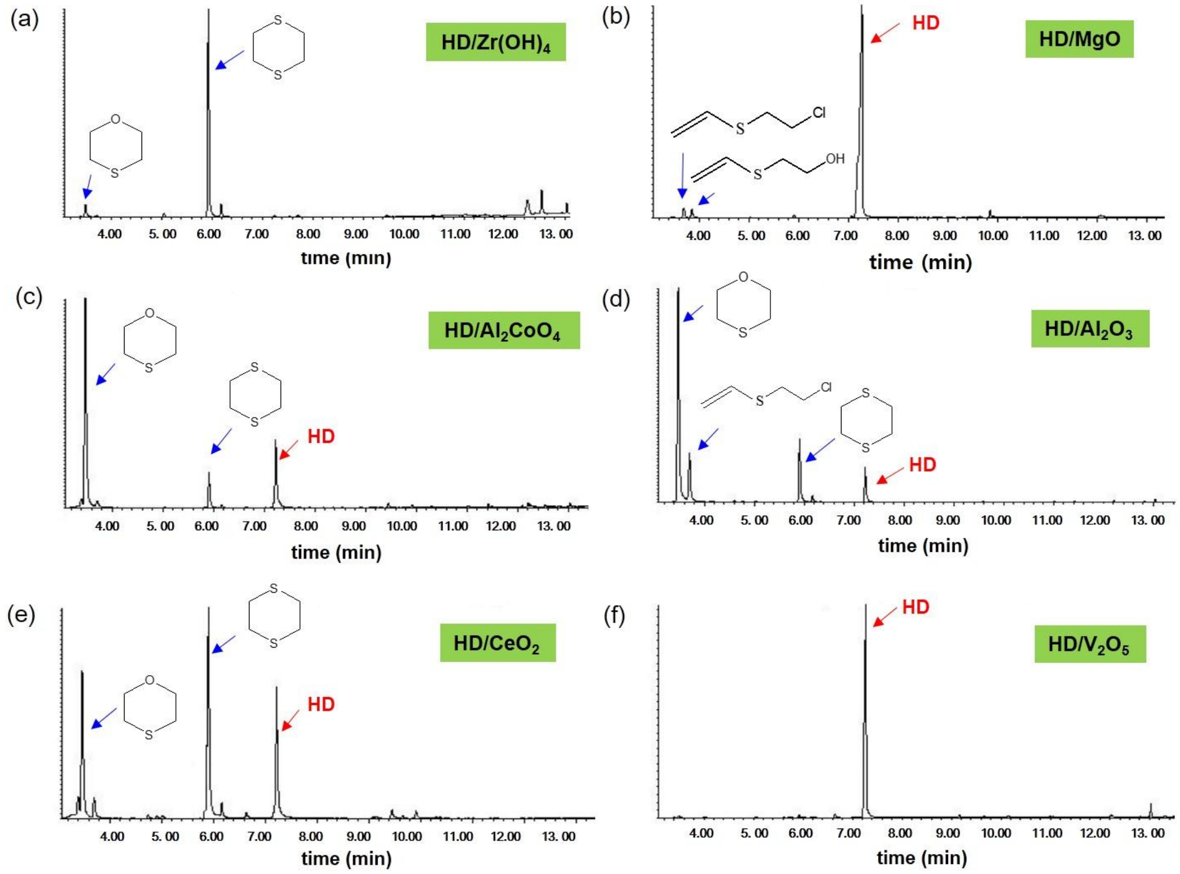


Figure 2 Chromatograms of thermally-degraded HD with the presence of various metal oxide adsorbents: (a) $Zr(OH)_4$, (b) MgO, (c) Al_2CoO_4, (d) Al_2O_3, (e) CeO_2, and (f) V_2O_5

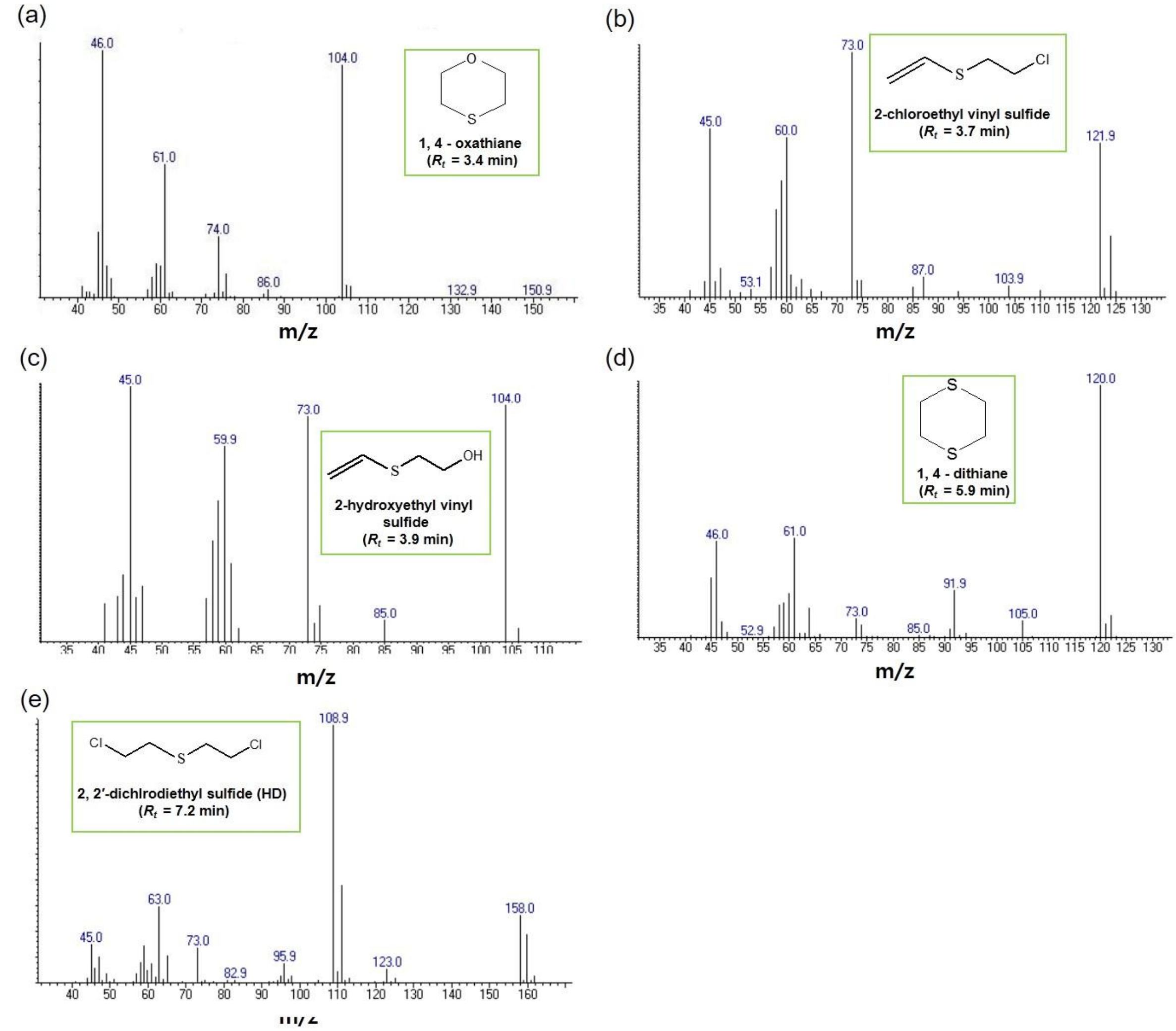


Figure 3 Mass spectra of (a) 1,4-oxathiane (R_t = 3.4 min), (b) 2-chloroethyl vinyl sulfide (R_t = 3.7 min), (c) 2-hydroxyethyl vinyl sulfide (R_t = 3.9 min), (d) 1,4-dithiane (R_t = 5.9 min), and (e) 2,2′-dichlorodiethyl sulfide or HD (R_t = 7.2 min)

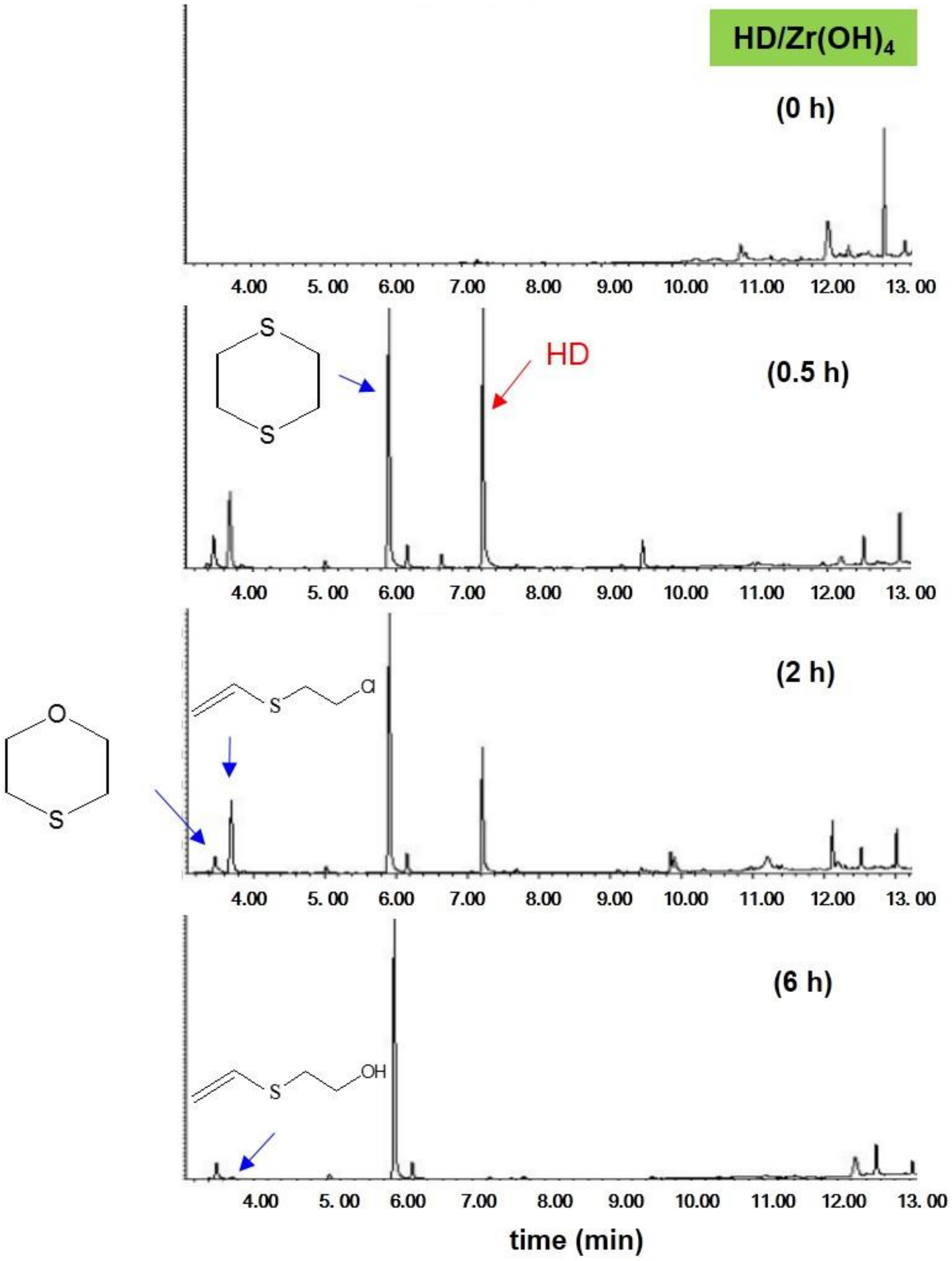


Figure 4 Thermal degradation profiles of HD with the presence of $Zr(OH)_4$ at different times

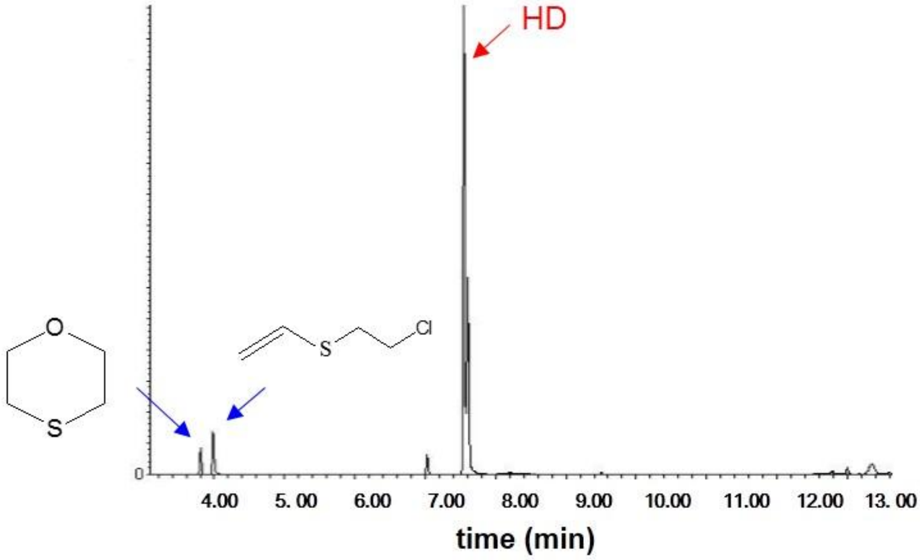
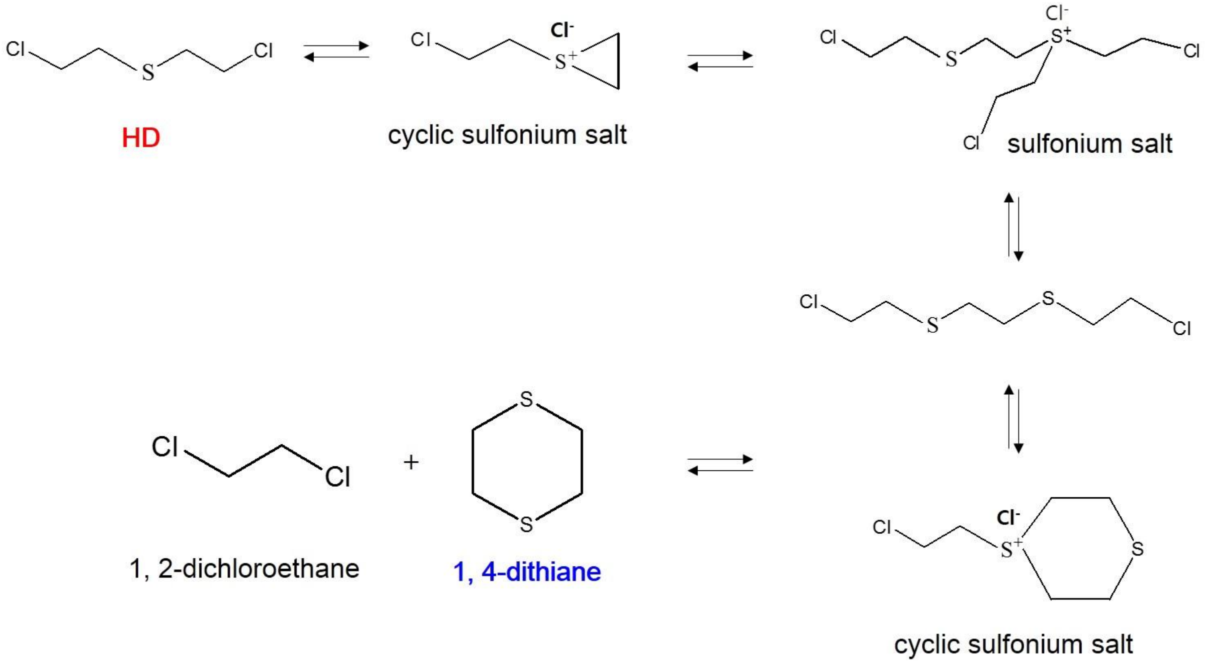
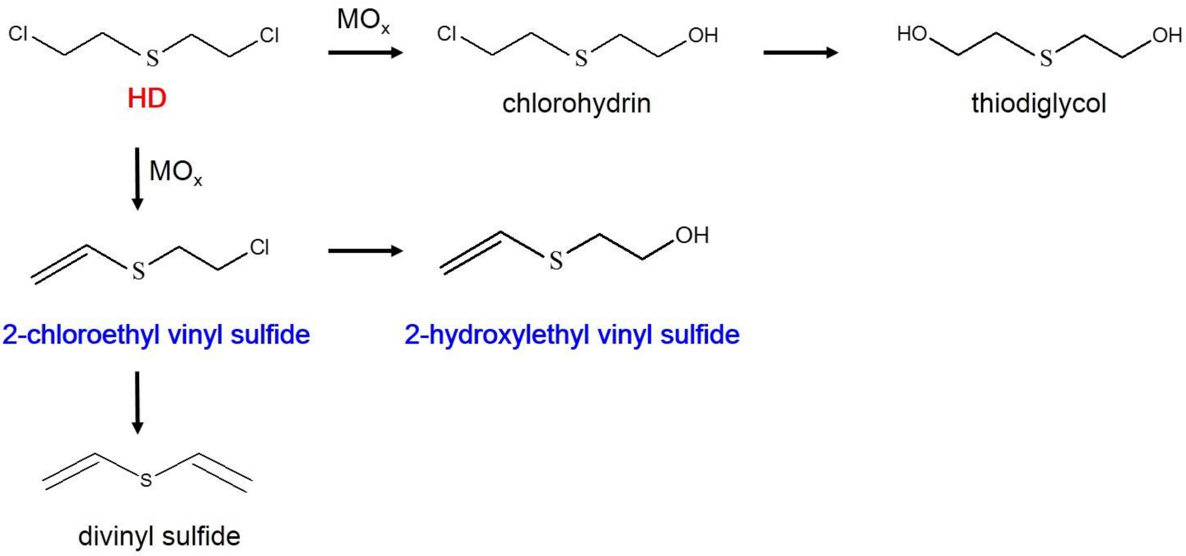


Figure 5 Chromatogram of HD with the presence of $Zr(OH)_4$ at room temperature without heating (6 h)

Scheme 1


HD
cyclic sulfonium salt
sulfonium salt
1, 2-dichloroethane
1, 4-dithiane
cyclic sulfonium salt

Scheme 2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S
Cl
HD
Cl
S
OH
chlorohydrin
HO
S
OH
thiodiglycol
MOx
S
Cl
2-chloroethyl vinyl sulfide
S
OH
2-hydroxylethyl vinyl sulfide
S
divinyl sulfide