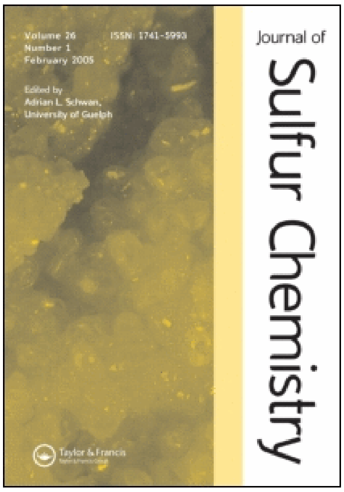

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Reaction of elemental sulfur in ethylenediamine with sulfur mustard

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Reaction of elemental sulfur in ethylenediamine with 1,1-thiobis(2-chloroethane) or sulfur mustard, the potent chemical warfare agent has been studied. The optimum conditions for the reaction are established for the complete conversion of sulfur mustard into non-toxic products. The above reaction has been successfully converted into a technology for chemical destruction of sulfur mustard (patented in USA, Russia, Germany and India).

Keywords: Elemental sulfur; Sulfur mustard; Ethylenediamine

1. Introduction

1,1'-thiobis-(2-chloroethane), commonly known as sulfur mustard (SM, 1) is a highly toxic and persistent liquid vesicant [1]. This thioether is one of the oldest and most important chemical warfare (CW) agents. It was used extensively in World War I and is a major item in stockpiles of CW agents manufactured [2–4]. Under the Chemical Weapon Convention (CWC) [5] which came into force in 1997, these stockpiles are required to be destroyed within 10 years of the convention, i.e. up to 2007.

One of the methods reported in the literature as well as widely used for large scale destruction of SM is high-temperature incineration [6]. However this method is opposed by environmentalists because toxic effluents are formed even in state-of-the-art incinerators [7–10]. In addition, there is always an unexplained fear that SM may be released in very minute quantities. For this reason much effort has been devoted towards the development of alternative technologies [11, 12]. Plasma treatment and electrochemical reduction are some of the methods [13, 14] being examined but are far from being used in practice.

Hydrolysis and oxidation [1, 15–18] are the preferred chemical methods for the decontamination of SM. However, SM is sparingly soluble in water, so hydrolysis of SM is difficult. Finally due to the formation of various products of hydrolysis comprising thiodiglycol, hydrochloric acid or chloride salts and organic sulfonium salts and generation of large volume

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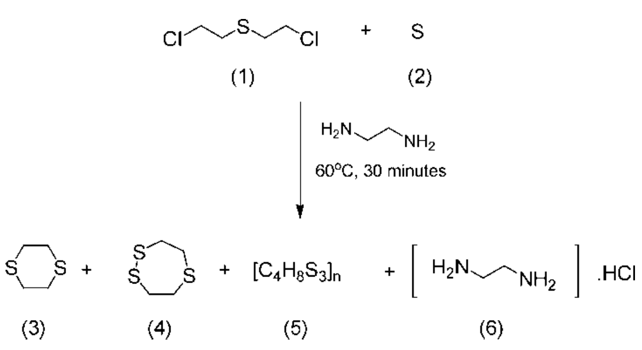
of liquid effluents, hydrolysis is not the method of choice for the destruction of the stockpile of SM. Secondly oxidation of SM produces the corresponding sulfone derivative which is also toxic [19], thus precluding this as a method of destruction from a CWC point of view. Other alternate technologies such as supercritical water oxidation or electrochemical reduction have not reached practical utility.

Global production of elemental sulfur is estimated to be 50–60 million metric tonnes on an annual basis, and is widely distributed on a regional basis, including North America, the Middle East, Europe and the former Soviet Union. This level of largely involuntary production has resulted in the increased attention focused on the use of elemental sulfur. Thus, we report here an alternative process [20] for the chemical conversion of sulfur mustard into non-toxic products quantitatively which involves the use of elemental sulfur in ethylenediamine (EDA). The reaction is simple, clean, efficient, and eco-friendly. From a CWC standpoint [21], the aim of our work was to develop a simple, efficient and irreversible chemical method for the destruction of SM stockpiles.

2. Results and discussion

Reactions of elemental sulfur in amines and ammonia are reported in the literature, where sulfur containing nucleophiles are produced [22–27]. We have carried out preliminary experiments by reacting SM with elemental sulfur in different aliphatic monoamines and diamines, and found that ethylene diamine (EDA) was found to be the best from the point of view of completion of reaction. The complete destruction of SM into non-toxic products was observed only by the reaction of SM with elemental sulfur in EDA. In this method, sulfur in EDA acts as a strong nucleophile [28] and reacts with SM leading to the formation of an oligomer $[C_4H_8S_3]_n$ (**5**) along with some other cyclic products *viz* 1,4-dithiane (**3**) and 1,2,5-trithiepane (**4**). The products were isolated and characterized by IR, NMR and GC-MS. The cyclic products and EDA hydrochloride (**6**) formed by the interaction of the solvent with liberated hydrogen chloride, are soluble in EDA but oligomer **5** is insoluble and so precipitates out immediately. The destruction efficiency of the reaction was found to be greater than 99.997% which was established on the basis of minimum detection limit of SM in EDA by GC/MS and was found to be 1 ppb (selected ion monitoring of the base peak ion of SM, m/z 109). The complete conversion of SM was also determined by the quantitative determination of **6** formed which is equivalent to the displaced chlorine from SM. The reaction sequence is given in Scheme 1.



SCHEME 1

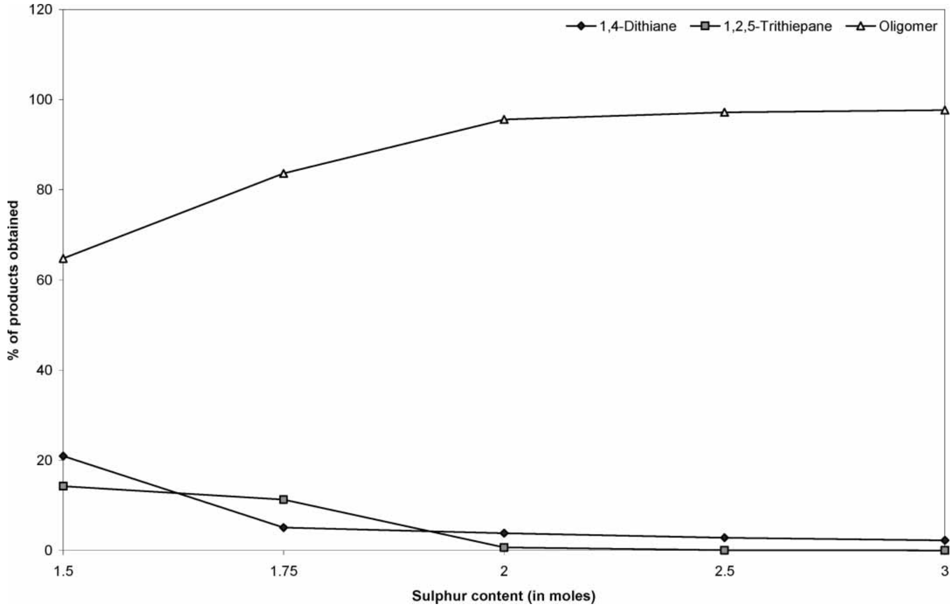


Figure 1. Effect of sulfur content on the formation of products in chemical destruction of SM using elemental sulfur in EDA at 60°C.

The reactions were carried out at temperatures ranging from 25–80°C and it was observed that the quantitative conversion of SM into non-toxic products took place in 30 minutes at 60 ± 5°C when the mole ratio SM:elemental sulfur was 1:2. Further it was observed that the increase in sulfur content reduced the formation of **3**and **4** and enhanced the formation of **5**. The results in figure 1 illustrate the effect of elemental sulfur content on the formation of reaction products.

Under the optimum reaction conditions (i.e. SM:S:EDA mole ratio, 1:2:24; reaction temperature, 60°C; and reaction time, 30 minutes), the ratio of products **3**:**4**:**5** were found to be 3.83:0.64:95.60 (w/w).

The above reaction was also applied for the destruction of other sulfur vesicants, like sesquimustard, which are generally present in SM stockpiles [29] and we found that similar products were formed on reaction with elemental sulfur in ethylenediamine.

In summary, we report herein the reaction of elemental sulfur in ethylenediamine with SM which is converted into a chemical process for the destruction of SM that realizes complete conversion into non-toxic products and provide advantages of easy, efficient, resource-saving, environmental and eco-friendly fulfilling the requirements of CWC. Moreover, this brings yet another advantage to the use of elemental sulfur in eliminating SM stockpiles.

3. Experimental

3.1 *Materials*

Commercial grade sulfur (>98% purity) and ethylenediamine (>98% purity) were used. Sulfur mustard was synthesized in-house by the procedure reported earlier [30] and its purity was greater than 98% by NMR and GC analysis. Caution: SM is a vesicant, carcinogen and cytotoxic agent. This compound should be handled in a fume cupboard (with a proper scrubbing system) by experienced persons with personal protective measures.

3.2 *Instruments*

Infrared (IR) spectra were recorded as KBr pellet using Perkin Elmer Spectrum BX FT-IR Spectrophotometer. Nuclear Magnetic Resonance (^{1}H NMR) spectrum was recorded on Bruker Avance 400 NMR. Gas chromatography-mass spectrometry (GC/MS) was performed using a Hewlett-Packard 6890 gas chromatograph equipped with a capillary column (30 m × 0.32 mm ID, 0.25 μm film thickness, BP-5 stationary phase, SGE) directly coupled to a Hewlett-Packard 5973 quadrupole mass spectral detector and integral data system. Ionization was done by electron impact at 70 eV and the source temperature was 230°C. The carrier gas was helium. Potentiometric titration using chloride ion selective electrode was used to find out chloride ion content in the product mixture.

3.3 *Experimental procedure*

In a 250 ml two-neck round bottom flask equipped with cold water condenser, calcium chloride guard tube and mechanical stirrer, ethylenediamine (161 ml, 2.4 moles) was taken. To this sulfur (6.4 g, 0.2 mole) was added with continuous stirring and then sulfur mustard (15.9 g, 0.1 mole) was added through a pressure-equalizing funnel. After the complete addition of SM, the reaction mixture was heated to to 60°C. After 30 minutes, the reaction mixture was cooled and filtered. The filtrate and the dichloromethane extract of the solid were analyzed by GC/MS by selected ion monitoring (m/z 109) to confirm the complete conversion of SM (All the experiments were conducted in fume hoods specially made for handling of toxic chemicals, and by personnel wearing protective equipment).

3.4 *Products analysis and estimation*

The product **3** and **4** were extracted from the filtrate of reaction mixture with dichloromethane, separated by column chromatography over silica gel with benzene:acetone (95:5 v/v) as eluent. Products were analyzed by IR, NMR and GC/MS and their structures were confirmed by comparison with spectral data of standard compounds.

3.4.1 1,4-Dithiane, 3. $C_4H_8S_2$, m.p. 112°C (Lit. 110–113°C), ^{1}H NMR ($CDCl_3$) δ, 2.90 ppm (s, 6H); MS (m/z) – 120 (M^+, 100), 46, 61, 92 [31, 32].

3.4.2 1,2,5-Trithiepane, 4. $C_4H_8S_3$, m.p. 74°C, b.p. 92–94°C/1 mmHg (Lit. 118–120°C/10 torr, 61–63°C/0.2 torr), ^{1}H NMR ($CDCl_3$) δ, 3.09 ppm (t, 4H, $-CH_2-S-CH_2$), δ 3.12 ppm (t, 4H, $-CH_2-S-S-CH_2$-); MS (m/z) – 152 (M^+, 100), 59, 45, 87, 124, 106 [33, 34].

The quantity of dithiane and 1,2,5-trithiepane were determined by Gas Chromatography with Flame ionization detector (packed column, OV-17, temp 180°C).

3.4.3 Oligomer, 5. Pale yellow amorphous solid, elemental analysis found C, 32.19; H, 5.48; S, 63.40 corresponding to $[C_4H_8S_3]_n$. The quantity of oligomer was determined by gravimetric analysis. It was insoluble in water and all the common organic solvents including carbon disulfide. Bulk density was found to be 0.882 at 25°C. Decomposition starts at 111°C (as determined by DSC). IR (KBr): 2921 cm^{-1} and 2852 cm^{-1} (CH_2 stretch); 1414 cm^{-1} (CH_2 bend); 1184 cm^{-1} (C−C). ^{13}C-NMR (solid) showed two absorption signals between δ 30 to 45 ppm indicating two different types of carbon atoms only. Further work is in progress to establish the structure and application(s) of the oligomer.

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