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HEAT CHARACTERISTICS OF CHEMICAL WARFARE AGENTS

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The heat characteristics of sulfur mustard (H), Lewisite (L), LI, LII, LIII, yellow agent (1:1 mass/mass H and L) and H heels were investigated by thermogravimetric – differential thermal analysis (TG-DTA). The object of this study was to provide details of the effectiveness of elevated temperature on the decomposition of these agents in both an active atmosphere (air) and an inert atmosphere (nitrogen). TG-DTA measured object mass change and heat radiation/absorption corresponding to regulated temperature changes of the test materials. All agents, with the exception of one of the H heels, exhibited an endotherm suggesting evaporation of the agents rather than oxidation.

Keywords: *chemical warfare agents, dimilitarisation, heat characteristics, TG-DTA*

Introduction

The Chemical Weapons Convention (CWC) entered into force in 1997 [1] and technologies are continuously being developed for the destruction of stockpiled and abandoned munitions filled with toxic agents. The CWC obligates all State Parties to safely destroy stockpiles of chemical weapons (CW) by 2007 [2]. With respect to percentage agent fill of munitions, an artillery round may typically contain 10% mass/mass agent and this is increased to around 60% for an aircraft bomb [3]. Russia and the US had the largest stockpiles of CW and agents anywhere in the world. In Russia, CW stores are dominated by nerve agents sarin, soman and VX and the vesicant agents mustard (H), Lewisite (L) and H–L mixtures, approx. 40 000 agent-tonnes in total [2, 4]. The US stockpiled Lewisite after World War I and H and L are included in the US unitary CW stockpile with an approx. total of 28 570 agent-tonnes [2, 5]. Up until the end of World War II, Germany manufactured 300,000 tons of chemical munitions [6]. During the past 40 years, more than 20 000 agent-tonnes of agent have been destroyed in a number of countries, over 80% of this has been destroyed by incineration [2].

This paper concentrates on the vesicant agents mustard (H), Lewisite (L) I–III (LI–III), yellow agent (1:1 mass/mass H–L) and H heels. Warfare use of vesicants decreases the opponent's ability to fight by producing chemical burns on tissues that come into contact with either vapours or liquid droplets/aerosols. Mustard is a viscous oily liquid with a boiling point of 217°C. It is also an alkylating agent with mutagenic effects [7]. It has a garlic like odour and has sufficient volatility that at ordinary temperatures, mustard vapour will be in the air immediately surrounding droplets of liquid mustard. Thus, the hazard of human contact is not only with droplets of liquid agent, but also with the agent vapours. Because of its low aqueous solubility, mustard agent is very persistent in the environment [8]. An individual exposed to blistering concentrations of mustard agent is incapacitated, often for weeks before returning to normal activity. Mustard has produced the greatest known number of chemically induced human casualties by far [9].

Lewisite is considered not only a lethal arsenical vesicant but also a systemic poison when absorbed into the bloodstream. Lewisite exposure causes immediate onset of pain, in direct contrast to the delayed pain reaction of mustard, which can be several hours [5, 8, 10]. Further information on the chemical and physical properties of CW agents are detailed in [11].

H heels are solid material isolated from mustard stored in munitions and containers which has settled at the bottom of the container/munition. Recent sampling of two containers from a mustard stockpile that had been in storage for over 50 years revealed that the amount of heel present can be as high as 20–30% of the total volume of the liquid mustard [12]. Characterisation of this solid is problematic, as it is a complex mixture of many compounds, probably higher molecular mass compounds due to the reaction of mustard with thiodiglycol type compounds. Stable sulfonium ions which have low volatility and thermally degrade to neutral species are therefore not detected by conventional gas chromatographic/mass spectrometric analysis. Some electrospray mass spectrometry analyses has successfully identified the major component of a mustard heel isolated from mus-

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tard storage ton containers as the 1-(2-chloroethyl)-1,4-dithianium ion [12].

The thermal degradation of mustard has been investigated previously [13] where it was found not to go to completion at 140°C due to the equilibrium existing between mustard and its products.

This study examined thermogravimetric – differential thermal analysis (TG-DTA) of H–L, LI–III, H–L (1:1) and H heels at 1000°C in order to gather oxidative decomposition data for CW incineration destruction technologies. TG-DTA measures the difference in temperature between a sample and reference material as a function of temperature when they undergo temperature scanning in a controlled atmosphere. The object mass change and heat radiation or absorption corresponding to regulated temperature changes of the test materials is measured. Thermal analysis methods have been used for a diverse range of studies; characterisation of oxidation products [14], carbon monoxide interactions [15] and ash content in municiple solid wastes [16]. The effectiveness of elevated temperature in both an active atmosphere (artificial air) and inert atmosphere (nitrogen gas) for the decomposition of these agents was determined.

Experimental

Materials

The agents investigated in this study are shown in Table 1. All agents excluding the H heels were synthesised in-house and characterised by gas chromatography-mass spectrometry (GC-MS), and nuclear magnetic resonance (NMR) spectroscopy to ensure the purity of each of these materials was not less than 98%. The Lewisite (L) used in the experiments contained a mixture of the three forms of Lewisite, LI–III (mass/mass ratio 73:26:1). H heels were supplied from old H munitions awaiting disposal.

Table 1 Compound names and abbreviations of all agents used in this investigation

Compound name	Synonym/abbreviation
bis(2-chloroethyl) sulfide	H, sulfur mustard
2-chlorovinyldichloroarsine	LI
bis(2-chlorovinyl) chloroarsine	LII
tris(2-chlorovinyl) arsine	LIII
LI, LII and LIII (mass/mass ratio 73:26:1)	L
H–L (mass/mass ratio 1:1)	yellow agent, H–L
complex heterogeneous system of unknown compounds	H heel

Instrument specifications

The TG-DTA system employed was a Setaram TGA-92 Thermoanalyser.

TG-DTA temperature was increased from 25°C at a rate of 20°C min^{-1} up to 900°C. This temperature was held for 2 min and increased to a final temperature of 1000°C at a rate of 2°C min^{-1}. 900°C was reached in 44 min and the final temperature of 1000°C was reached in 108 min.

Reference materials

Reference materials (lead and tin) were supplied by Aldrich, Poole UK (99.99% purity), indium wire supplied by Alfa, Johnson Matthey Materials Technology UK, (99.998% purity).

TG-DTA experimental runs

Approximately 30–60 mg (113 mg for H heel 3 in air) of test material was used for each experiment. Each agent was tested in an active and inert atmosphere at a rate of 50 mL min^{-1}. Mass changes of the test materials and the state of heat radiation/absorption corresponding to temperature rises was continuously monitored. A total of twenty-four TG-DTA experiments were performed and are detailed in Table 2.

Results and discussion

Results of all the CW agents tested in air and nitrogen, including initial and residual masses, exhibition of an endotherm or exotherm, temperature and approximate time at the end of evaporation are summarised in Table 3.

Discussion of all agents excluding H heels

As can be seen from Table 3, none of the agents tested left any residual masses at the end of the TG-DTA runs, indicating that all of the samples were evaporated.

Figure 1 is indicative of the profile exhibited in the H experiments. All agents displayed an endotherm demonstrating the agents were evaporated rather than decomposed. The lack of exotherms suggests no oxidative decomposition took place.

All agents completed evaporation by 305°C. There did not appear to be considerable difference in evaporation completion temperatures for all the agents between air and nitrogen (200–305 and 202–285°C, respectively). Of all the agents, LIII completed evaporation at the highest temperature in both air and nitrogen (305 and 285°C, respectively).

Table 2 TG-DTA experiments to investigate the heat characteristics of H, L, LI, LII, LIII, yellow agent and H heels

Expt. no.	H/mg	L/mg	LI/mg	LII/mg	LIII/mg	Yellow agent/mg	H heel 1/mg	H heel 2/mg	H heel 3/mg	Active (A) or inert (I) atmosphere	Notes
1	30	–	–	–	–	–	–	–	–	A	
2	30	–	–	–	–	–	–	–	–	A	duplicate
3	30	–	–	–	–	–	–	–	–	I	
4	30	–	–	–	–	–	–	–	–	I	duplicate
5	–	30	–	–	–	–	–	–	–	A	
6	–	30	–	–	–	–	–	–	–	A	duplicate
7	–	30	–	–	–	–	–	–	–	I	
8	–	30	–	–	–	–	–	–	–	I	duplicate
9	–	–	30	–	–	–	–	–	–	A	
10	–	–	30	–	–	–	–	–	–	I	
11	–	–	–	30	–	–	–	–	–	A	
12	–	–	–	30	–	–	–	–	–	I	
13	–	–	–	–	30	–	–	–	–	A	
14	–	–	–	–	30	–	–	–	–	I	
15	–	–	–	–	–	30	–	–	–	A	
16	–	–	–	–	–	30	–	–	–	A	duplicate
17	–	–	–	–	–	30	–	–	–	I	
18	–	–	–	–	–	30	–	–	–	I	duplicate
19	–	–	–	–	–	–	30	–	–	A	
20	–	–	–	–	–	–	30	–	–	I	
21	–	–	–	–	–	–	–	30	–	A	
22	–	–	–	–	–	–	–	30	–	I	
23	–	–	–	–	–	–	–	–	30	A	
24	–	–	–	–	–	–	–	–	30	I	

Table 3 Summary of TG-DTA results for H, L, LI, LII, LIII, yellow agent and H heels

Agent experiment	Initial mass/mg	Residual mass/mg	Endotherm or exotherm?	Temperature at end of evaporation/°C	Approx. time at end of evaporation/min
Active atmosphere (air)					
H	31.7	0.0	endotherm	235	14.0
H duplicate	34.3	0.0	endotherm	242	14.0
L	49.7	0.0	endotherm	250	14.0
L duplicate	49.6	0.0	endotherm	225	14.0
LI	51.3	0.0	endotherm	200	13.0
LII	45.7	0.0	endotherm	255	13.0
LIII	59.1	0.0	endotherm	305	16.5
Yellow agent	43.0	0.0	endotherm	244	14.0
Yellow agent duplicate	39.3	0.0	endotherm	233	14.0
H heel 1	36.2	0.8	endotherm (×2)	620	32.5
H heel 2	39.1	1.3	none	530	37.5
H heel 3	113.0	8.5	endotherm (×2)	508	27.5
Inert atmosphere (nitrogen)					
H	47.3	0.0	endotherm	232	14.5
H duplicate	34.5	0.0	endotherm	251	14.5
L	48.6	0.0	endotherm	202	12.7
L duplicate	49.4	0.0	endotherm	228	13.0
LI	51.7	0.0	endotherm	208	13.0
LII	47.0	0.0	endotherm	244	15.0
LIII	42.4	0.0	endotherm	285	16.3
Yellow agent	40.7	0.0	endotherm	246	14.0
Yellow agent duplicate	39.2	0.0	endotherm	237	14.0
H heel 1	32.5	2.2	endotherm (×2)	846	50.0
H heel 2	35.6	7.6	endotherm	910	50.0
H heel 3	32.7	2.4	endotherm	715	45.0

All agents (except LIII) completed evaporation in approx. the same time, between 13 and 15 min in both air and nitrogen. LIII took slightly longer to complete evaporation in air and nitrogen (16.5 and 16.3 min, respectively). The higher evaporation temperature and increased evaporation time for LIII may be because LIII is a solid at ambient temperature and has to be melted prior to evaporation. All the other agents in this group are liquids at ambient temperatures.

Discussion of H heels

From Table 3, the only agents to have any residual masses at the end of the TG-DTA runs were the H heels (Figs 2–7). This may be because H heels are complex heterogeneous systems comprising higher molecular mass compounds, probably due to the reaction of H with thiodiglycol type compounds. Residual masses for H heel 1 in the active and inert atmospheres were relatively constant, however residual masses for H heel 2 in the active and inert atmospheres were very different (1.3 and 7.6 mg, respectively). H heel 3 had more residual mass in the active atmosphere compared to the inert atmosphere. These varying masses of residual material may be due to the H heels not being homogeneous; therefore the samples may have been different parts of the same H heel exhibiting assorted heat characteristics. The residue remaining may be metal salt or metal oxide contamination from the shell.

H heels 1 and 3 in air (Figs 2 and 4, respectively) showed two different components being evaporated at two different temperature zones and the heat flow

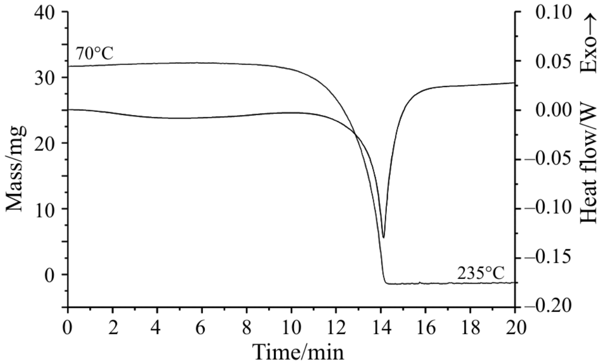

Fig. 1 TG-DTA of H in air

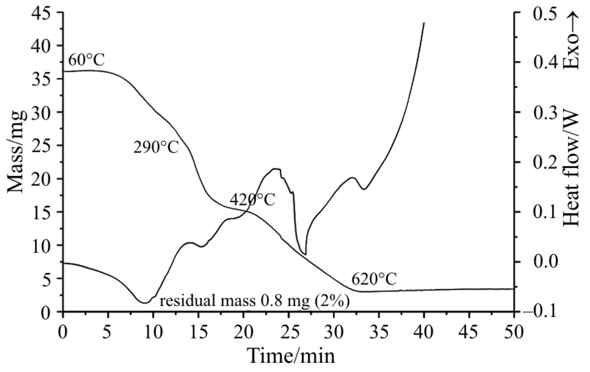

Fig. 2 TG-DTA of H Heel 1 in air

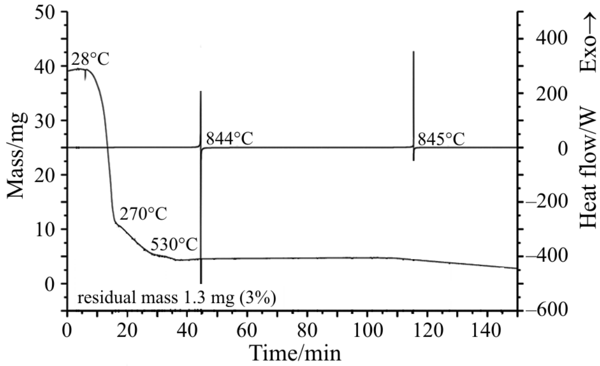

Fig. 3 TG-DTA of H Heel 2 in air

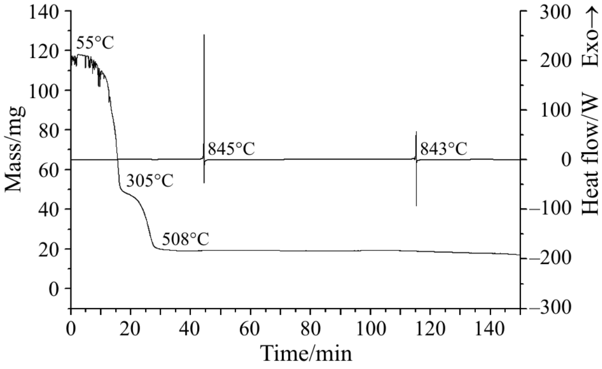

Fig. 4 TG-DTA of H Heel 3 in air

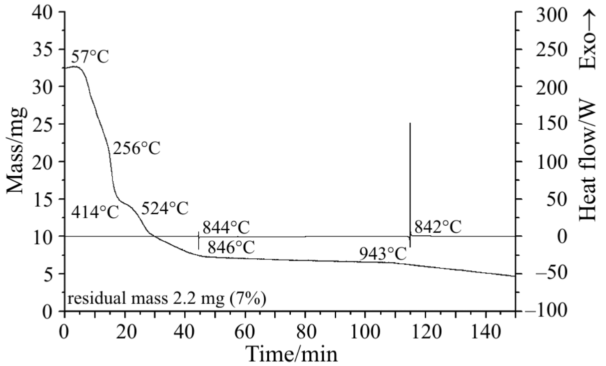

Fig. 5 TG-DTA of H Heel 1 in nitrogen

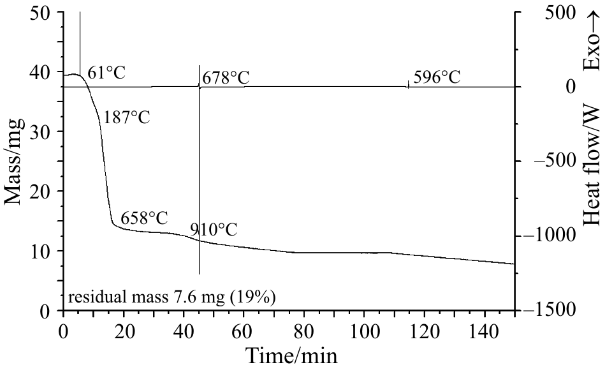

Fig. 6 TG-DTA of H Heel 2 in nitrogen

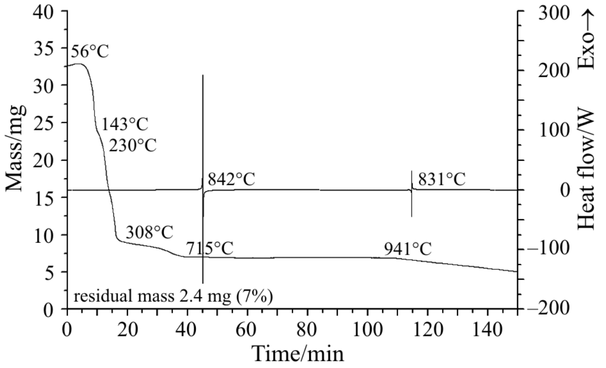

Fig. 7 TG-DTA of H Heel 3 in nitrogen

lines indicated two endotherms, suggesting evaporation of the components rather than oxidative decomposition. H heel 2 in air (Fig. 3) showed two different components being evaporated at two different temperature zones, but the heat flow line did not indicate any endo/exotherms. H heel 2 may be more pure than H heels 1 and 3 because the mass loss line was less complicated in both air and nitrogen. There was no convincing evidence of any exotherms in either of the atmospheres. H heels are far from simple pure components, rather they are complex mixtures and these differences may be attributed to the unique nature of each sample tested.

H heel 1 in nitrogen (Fig. 5) did not appear to be different from H heel 1 in air. H heels 2 and 3 in nitrogen (Figs 6 and 7, respectively) did not differ appreciably to H heels 2 and 3 in air, except for the appearance of one small endotherm under nitrogen gas. These features indicated evaporation of the H heel components rather than oxidation. The slight difference in behaviour of H heels 1–3 is probably due to the heterogenous nature of samples in this study.

H heels exhibited complete evaporation at higher temperatures in both atmospheres compared to all the other agents tested. Under air, evaporation was complete by 620°C but under nitrogen the temperature was higher (910°C). This increased temperature in both types of atmosphere may be because H heels are complex heterogeneous systems, comprising higher molecular mass compounds. H heels exhibited longer evaporation completion times compared to the other agents tested. H heel evaporation times in air were 27.5–37.5 min and 45–50 min in nitrogen.

Conclusions

Of all the agents tested, in both atmospheres, only H heels left residual masses at the end of the TG-DTA runs, possibly due to H heels being complex heterogeneous systems, comprising higher molecular mass compounds and metal impurities.

All agents tested in both atmospheres (with the exception of H heel 2 in air) exhibited an endotherm, demonstrating evaporation of the agent rather than decomposition. No agents displayed exotherms suggesting evaporation dominates heat characteristics compared to oxidation. All H heels showed two different components evaporating at two different temperature zones in both atmospheres. H heels completed evaporation at higher temperatures and at longer evaporation times in both atmospheres compared to all the other agents tested.

All agents (except H heels) completed evaporation by 305°C within 16.5 min, in both atmospheres.

LIII had a slightly higher evaporation temperature and evaporation completion time compared to the other agents (except H heels), possibly due to it being a solid at ambient temperature.

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