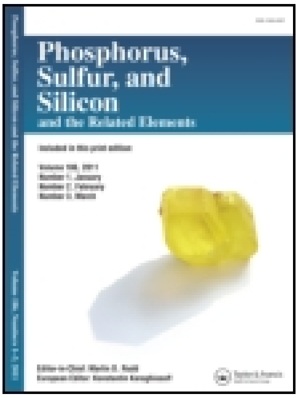

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L-Gel Formulation and Decontamination Reaction of Its Active Ingredient (Oxone) Against Mustard and VX Nerve Agent Simulants

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L-GEL FORMULATION AND DECONTAMINATION REACTION OF ITS ACTIVE INGREDIENT (OXONE) AGAINST MUSTARD AND VX NERVE AGENT SIMULANTS

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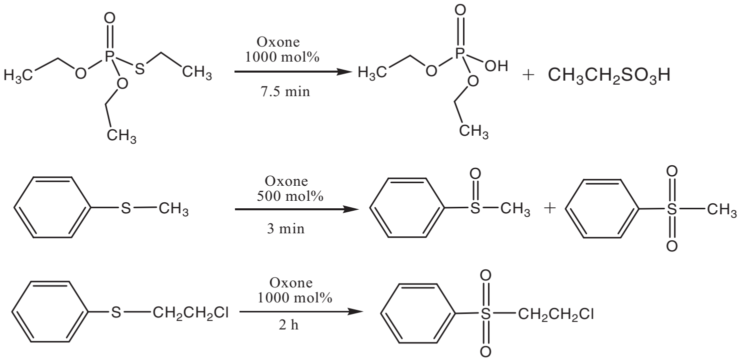
GRAPHICAL ABSTRACT



Abstract *L-Gel is an effective decontamination reagent against chemical and biological warfare agents. To achieve optimized formulation of L-Gel, several formulations with different proportional amounts of oxone (oxidizer) and Cab-O-Sil (gelling agent) were prepared and their viscosities and densities were measured. Final optimized formulation of gel was obtained as a 0.25 M aqueous solution of oxone gelled with 13%W/W of Cab-O-Sil EH-5. The L-Gel active ingredient (oxone) was tested against O,O,S-triethyl phosphorothioate (TEPT) as VX simulant and methyl phenyl sulfide (MPS) and chloroethyl phenyl sulfide (CEPS) as HD simulants. Decontamination of TEPT by a 10-fold excess amount of oxone was completed within 7.5 min with a kinetic rate constant of 0.097* S^{-1}. *In the presence of oxone, MPS was converted to methyl phenyl sulfoxide and methyl phenyl sulfone with a higher reaction rate than CEPS, decontaminated product of which was chloroethyl phenyl sulfone.*

Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.*

Keywords L-Gel; oxone; Cab-O-Sil EH-5 fumed silica; decontamination; VX nerve agent simulant; mustard simulant

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INTRODUCTION

Decontamination is an essential process and an important step to be taken in to account with the chemical and biological agents. Different decontamination methods and procedures such as liquids, foams, gels, gaseous, and vapor techniques exist to neutralize and detoxify chemical and biological warfare agents.[1–15] Foam and gel technologies are designed to enhance surface removal of biological or chemical contaminants by delivering the decontamination formulation in a matrix that can be applied on vertical and horizontal surfaces. This allows the application to walls with sufficient contact time to ensure that the chemical and biological agents are effectively treated and consist of systems such as CASCAD and L-Gel.[9,10]

Due to its nontoxic, noncorrosive, and high-rate decontamination nature, L-Gel is a suitable decontamination reagent to be used for military and civilian purposes and it exerts minimal damage to the environment.[9] L-Gel has three important characteristics: it oxidizes the chemical warfare agents; kills the bacterial spores used as biological warfare agents; and sticks to vertical and overhead surfaces.

L-Gel consists of two principal ingredients: the oxidizing and the gelling agent. The oxidizing agent in L-Gel is oxone, a triple salt with the formula $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$. Oxone is a nonchlorine alternative used as a decolorizer and disinfectant and has shown effective reaction with chemical warfare agents.[10] The active ingredient in oxone is potassium peroxymonosulfate "$KHSO_5$." The peroxymonosulfate anion is a moderate strength oxidizer that contributes an electron to the chemical bonds of the target compound and disrupts the bonds.

The gelling agent in L-Gel is Cab-O-Sil EH-5 fumed silica (synthetic amorphous colloidal silica). High purity, aggregated structure, submicron particle size, low bulk density, high surface area (380 m^2/g), and hydrophilic surface are the advantages of EH-5 over other Cab-O-Sil grades. Cab-O-Sil EH-5 has an average particle length of 0.2–0.3 μm with very high surface area and can increase the viscosity of liquid system.[14]

L-Gel is packaged as a high-viscosity, gelatin-like semisolid that is liquefied by shaking or stirring.[9] The liquefied product can be applied using paint spraying equipment that is commercially available. Due to L-Gel's acidic properties, stainless steel spray nozzles must be used.

Most of the toxic organophosphorus esters can be detoxified quickly by hydrolysis in alkaline solution. However, the hydrolysis of phosphonothiolate esters as VX is much slower and ineffective even at very high pH.[7] However, oxidation of the sulfur in VX in aqueous acid solution is rapidly followed by hydrolysis to nontoxic products. An acidic solution also causes protonation of the amine nitrogen, increasing the solubility of VX and enhancing the oxidation of sulfur.[7,9,12] Oxone has shown the ability to oxidize VX to ethyl methanephosphonic acid and diisopropyl taurine.[1]

$$\begin{aligned} &\mathrm{MePO(OEt)SCH_2CH_2N(}i\,\mathrm{Pr)_2} + 3\ \mathrm{KHSO_5} + \mathrm{H_2O} \\ &\quad \rightarrow \mathrm{MePO(OEt)OH} + \mathrm{HO_3SCH_2CH_2N(}i\,\mathrm{Pr)_2} + 3\ \mathrm{KHSO_4} \end{aligned}$$

Dissolution of sulfur mustard into water is slow. Thus hydrolysis is not very effective against it and sulfur mustard detoxification in aqueous solution must be performed via oxidation.[1] Oxidation of an organosulfide (RR′S) by hydrogen peroxide can produce two oxidation products, the sulfoxide (RR′SO) and the sulfone ($RR'SO_2$), under different reaction conditions.[15–21] Thus, the decontamination products of HD via oxidation are sulfoxide (HDO) and sulfone (HDO_2). The sulfoxide is nonvesicant and quite stable toward hydrolysis, whereas the sulfone still retains appreciable vesicant activity and is prone to slow hydrolysis. Thus, HD can be rendered nonvesicant via selective oxidation to the sulfoxide.[13] In this study, L-Gel formulation and its decontamination effects on VX and mustard simulants have been investigated.

RESULTS AND DISCUSSION

Preparation of Optimized L-Gel Formulation

In order to achieve optimized formulations of L-Gel, the effects of various factors such as presence of air, stirring rate, amount of Cab-O-Sil EH-5 and oxone on the gel properties were investigated. The rate and time of stirring are important, as a result of which Cab-O-Sil EH-5 molecules are surrounded by solvent and a three-dimensional lattice gel is formed. The time required for lattice completion was 30 min. Continuation of stirring beyond 30 min caused the lattice to be disrupted and the viscosity to be decreased. This observation is related to the thixotropy property of gel. In the absence of air, the viscosity of samples decreases faster, therefore the presence of air is important in gel formation. If the sample is left unaltered for several hours, its viscosity increases again.

The Gel quality is influenced and controlled by the amount of Cab-O-Sil. If the Cab-O-Sil percent is less than 8% w/w, the resulting gel is unstable and diphasic. At over 8% w/w, the resulting gel is stable and mono phase even at high-speed centrifugal action. By increasing the amount of Cab-O-Sil, the viscosity increases and reaches a maximum for an amount of 13% w/w. Beyond 13% w/w, the trend of changes is switched and the viscosity drops down. Stirring the viscose gel at an early stage caused the viscosity to be reduced dramatically. This issue claims that the lattice gel initially suffered a sudden collapse but in continuation, the trend became slower (Figure 1).

Decontamination of *O,O,S*-Triethyl Phosphorothioate

Oxone reacted with *O*,*O*,*S*-triethyl phosphorothioate (TEPT) as an insoluble organic phase and entirely dissolved it. The reaction was exothermic and a lot of heat was librated. Comparison of ^{31}P and ^{13}C NMR spectra of pure TEPT in $CDCl_3$ and reaction mixture of 0.001 mol of TEPT and 1000 mol% of oxone in aqueous solution after 7.5 min showed the

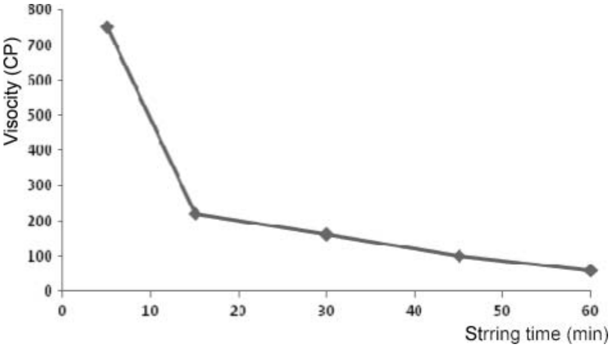


Figure 1 The effect of stirring time on the viscosity of L-Gel.

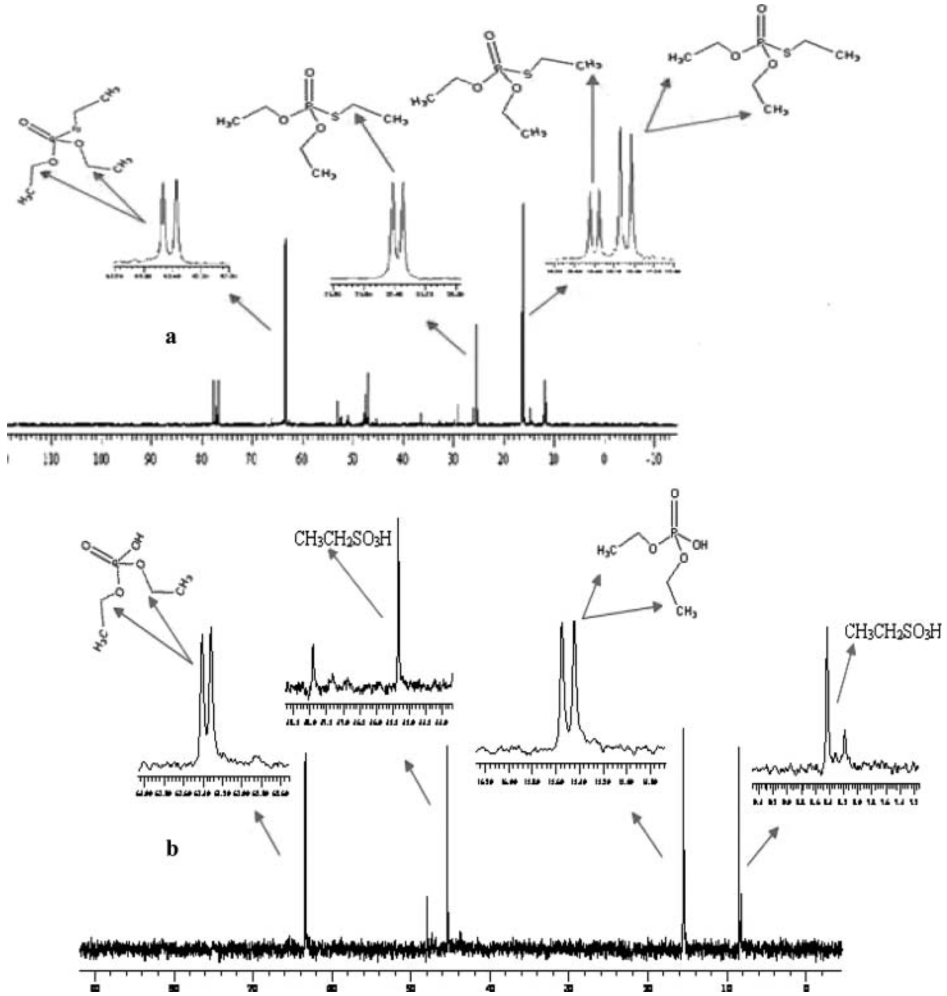
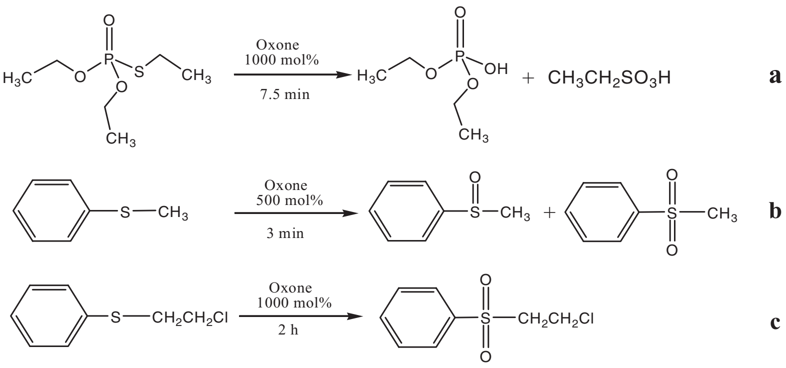


Figure 2 ^{13}C NMR spectra of TEPT in $CDCl_3$ (a) and of TEPT (0.001 mol) in aqueous solutions of oxone (1000 mol%) after 7.5 min (b).

formation of novel compounds. According to the ^{31}P NMR spectra, the reaction of oxone with TEPT ($\delta = 28.3$ ppm) was completed after 7.5 min and a pentagon peak appeared at 1.2 ppm which indicates the conversion of TEPT to phosphoric acid diethyl ester (i.e., $(EtO)_2POOH$). Considering the ^{13}C NMR spectra (Figure 2), $CH_3CH_2SO_3H$ is another product formed by the reaction of oxone with TEPT in aqueous solution (Scheme 1a).

To study the kinetics of TEPT decontamination reaction, three experiments with different concentrations of oxone were carried out (Table 1). At excess amount of oxone a linear behavior of $\ln([TEPT]_0/[TEPT])$ versus time with a k_{obs} value of 0.097 s^{-1} was observed showing a pseudo first-order decontamination of TEPT in the presence of excess amounts of oxone. At 250 mol% of oxone, the reaction had a suitable rate at the beginning but as the reaction went on, the progress was not notable because in order to decontaminate 1 mol of TEPT, 3 moles oxone were needed. Therefore, the amount of oxone was reduced after 15 min and the rate of reaction became slower. After 70 min, all the oxone in the



Scheme 1

reaction mixture were consumed and the reaction was halted so the composition of the reaction mixture remained constant.

Table 1 Decontamination of TEPT in the presence of 250, 500 and 1000 mol% of oxone after different reaction times according to the ^{31}P NMR spectra

Oxone (mol%)	Reaction time (min)	$(CH_3CH_2O)_2PO(SCH_2CH_3)$ ^{31}P NMR $\delta = 28.3$ ppm (%)	$(CH_3CH_2O)_2POOH$ ^{31}P NMR $\delta = 1.2$ ppm (%)
250	5	58	42
	15	42	58
	130	32	68
500	7.5	19	81
	15	10	90
	25	4	96
1000	5	6	94
	7.5	0	100

Decontamination of Methyl Phenyl Sulfide

Chromatographic comparison of pure methyl phenyl sulfide (MPS) (retention time of ~9 min) and the reaction mixture of MPS with oxone (500 mol%) after 3 min showed that MPS was oxidized and converted to two compounds with retention times of ~14 and ~16 min (Scheme 1b). The same compounds were found as the decontamination products of MPS by activated hydrogen peroxide with the same GC characteristics and were identified by GC-MS analysis as methyl phenyl sulfoxide [MPSO; retention time: 6.9 min; m/z (%): 41(17), 43(10), 45(25), 50(36), 51(68), 53(23), 55(12), 65(19), 77(50), 81(11), 94(24), 97(87), 124(20), 125(83), 140(100), 141(24)] and methyl phenyl sulfone [$MPSO_2$; retention time: 8.1 min; m/z (%): 50(22), 51(47), 65(16), 77(100), 93(12), 94(51), 141(29), 156(31)] as was reported previously for the oxidation of MPS with activated hydrogen peroxide.[15]

Decontamination of Chloroethyl Phenyl Sulfide

GC analysis of the reaction mixture of chloroethyl phenyl sulfide (CEPS) with oxone (1000 mol%) extracted by CH_2Cl_2 states that 90% of CEPS (retention time of ~16 min) is eliminated after 2 h and a new product with a retention time of ~18 min is formed (Scheme 1c). The decontamination product shows a ^{1}H NMR spectrum with two triplets at 3.55 and 3.75 ppm ($\Delta\delta = 0.20$ ppm) attributed to two CH_2 groups which are characteristic of chloroethyl phenyl sulfone conform on the prediction of the Chem Office software which predicts the chemical shift of two triplet in the ^{1}H NMR spectra as 3.05 and 3.75 for chloroethyl phenyl sulfoxide ($\Delta\delta = 0.70$ ppm) and as 3.70 and 3.95 for chloroethyl phenyl sulfone ($\Delta\delta = 0.25$ ppm). GC-MS analysis of the reaction mixture of CEPS with oxone (1000 mol%) extracted with CH_2Cl_2 showed a decontamination product with a retention time of 9.2 min and fragmentation pattern with m/z (%, fragment) of 205 (28, $C_6H_5SO_2CH_2CH_2Cl$), 156 (14, $C_6H_5SO_2CH_2$), 141 (100, $C_6H_5SO_2$), and 125 (27, C_6H_5SO) demonstrating the structure of decontamination product as chloroethyl phenyl sulfone.

CONCLUSION

In conclusion, L-gel containing less than 8% w/w of Cab-O-Sil is unstable and diphasic but over 8% w/w of Cab-O-Sil it is stable and forms a single phase. The optimum amount of Cab-O-Sil to form a stable gel with a suitable viscosity is 13% w/w. The optimized time of stirring to form a lattice gel is 30 min, after when, leaving the gel unaltered, it gradually starts to get viscous. The decontamination of TEPT with 1000 mol% of oxone in aqueous solution occurred after 7.5 min following a pseudo first-order reaction with k_{obs} value of 0.097 s^{-1} with apparition of diethyl phosphite ($(EtO)_2POOH$) and $CH_3CH_2SO_3H$ as the decontamination products. MPS in the presence of excess amounts of oxone (500 mol%) after 3 min was oxidized and converted to MPSO and $MPSO_2$. The reaction rate of CEPS with oxone was slower and decontamination of CEPS in the presence of 1000 mol% of oxone occurred after 2 h producing chloroethyl phenyl sulfone as the decontamination product. Additional studies should be done at a facility able to handle the real VX and HD agent to truly understand the overall effectiveness of such decontamination reagent.

EXPERIMENTAL

Viscometer DV-II + Pro Brookfield was used to determine the viscosities. NMR spectra were obtained on a Bruker ADVANCE DPX-250 instrument (250 MHz for ^{1}H NMR, 62.5 MHz for ^{13}C NMR and 100 MHz for ^{31}P NMR), and $CDCl_3$, and D_2O were used as solvents; chemical shifts are reported in δ (ppm) from TMS for ^{13}C and H_3PO_4 for ^{31}P. Gas chromatograms (GC) spectra were recorded on a Varian STAR 3400CX with a packed column (10% OV-101 CWHP 80/100, 2 m × 1.8″) and a He flow rate of 10 mL/min. Electron ionization GC-MS spectra were recorded on a Varian (SATURN 4D) spectrometer using an ionization current of 8 μA with a capillary column (DB-5MS, 0.1 μm, 30 m × 0.250 mm). Only m/z values having intensities of more than 10% are given. Retention times for GC and GC-MS were reported using temperature programming (100°C–250°C, 5°C/min for GC and 10°C/min for GC-MS) with $T_{col} = T_{inj} = 210°C$. MPS, CEPS, and TEPT were synthesized in our laboratory with a purity of >95%.

Preparation of Optimized L-Gel Formulation

Cab-O-Sil EH-5 (2.6 g, 13% w/w) was gently added to the stirred aqueous solution of oxone (2.29 g (0.0037 mol) of oxone dissolved in 15 mL of water). Stirring was continued for 30 min. If we are in a rush to use L-Gel, we should leave the gel to stand for 1 h to be in contact with air without stirring until the three-dimensional lattice gel is formed and the viscosity reaches the maximum. Aged gel should be stirred by a mechanical mixer prior to use, so that it becomes less viscous.

Decontamination Study of *O,O,S*-Triethyl Phosphorothioate

TEPT and an aqueous solution of oxone were directly mixed in an NMR tube and ^{31}P NMR spectrum was studied during the time.

Decontamination Study of Methyl Phenyl Sulfide and Chloroethyl Phenyl Sulfide

A total of 0.0001 mol (0.012 g) MPS was added to 1 mL of 0.5 M oxone solution (0.08 g, 500 mol%). The mixture was stirred and after 3 min the sample was extracted by CH_2Cl_2 and analyzed by GC and GC-MS.

A total of 0.0002 mol (0.034 g) CEPS was added to 1 mL of a 2M solution of oxone (0.3 g, 1000 mol%). The mixture was stirred and, after 30 min, one-half part of the sample was extracted with CH_2Cl_2 and was analyzed by GC. The second part of the mixture was stirred for 1.5 h and the sample was extracted with CH_2Cl_2 and analyzed by GC and GC-MS.

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