



Heriot-Watt University
Research Gateway

Scavenging Alkyl Mercaptans

Citation for published version:

Wylde, JJ, Taylor, GN, Sorbie, KS & Samaniego, WN 2020, 'Scavenging Alkyl Mercaptans: Elucidation of Reaction Mechanisms and Byproduct Characterization', *Energy and Fuels*, vol. 34, no. 11, pp. 13883–13892. <https://doi.org/10.1021/acs.energyfuels.0c02652>

Digital Object Identifier (DOI):

[10.1021/acs.energyfuels.0c02652](https://doi.org/10.1021/acs.energyfuels.0c02652)

Link:

[Link to publication record in Heriot-Watt Research Portal](#)

Document Version:

Peer reviewed version

Published In:

Energy and Fuels

Publisher Rights Statement:

This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Energy and Fuels*, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <https://doi.org/10.1021/acs.energyfuels.0c02652>

General rights

Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please contact open.access@hw.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Scavenging Alkyl Mercaptans: Elucidation of Reaction Mechanisms and By-Product Characterization

Wylde, J.J.^{a,b}, Taylor, G.N.^b, Sorbie, K.S.^a and Samaniego, W.N.^b

^aHeriot Watt University, UK; ^bClariant Corporation, US

ABSTRACT

The removal of alkyl mercaptans via chemical means in the oil and gas industry has received very little attention compared with the much more extensive work on hydrogen sulphide (H₂S) scavenging. It has been known for some time that mercaptan scavenging is possible but anecdotally reported as being less effective than H₂S scavenging.

This current study seeks to improve the understanding of the efficacy and mechanism of mercaptan scavenging by the common H₂S scavengers in use today. A thorough literature review is provided of the current state of the art in mercaptan scavenging. For the first time, a systematic series of quantified scavenging performance results for a variety of prominent scavengers with volatile alkyl mercaptans has been presented using the well-known autoclave method. These results are directly compared with the corresponding values for H₂S under identical reaction conditions; overall, the best product was to be 1,3,5-trimethylhexahydrotriazine (MMA-triazine).

The chemical structures of the reaction byproducts with alkyl mercaptans, to date only suggested but never confirmed, have been proven by the application of rigorous analytical methods. Results for both MMA-triazine and 1,3,5-tris(2-hydroxyethyl)hexahydro-s-triazine (MEA-triazine) reactions with ethyl, propyl and butyl mercaptan comprehensively show, via the use of GCMS(-EI) analysis, representatives from each step in the sequential reaction pathway, containing each 1, 2 and 3 nitrogen atoms showing definitively evidence for the proposed reaction pathway.

INTRODUCTION

In the oil and gas industry, numerous sulphur containing species occur in produced fluids and gases. These species are derived from geological and biological processes, and include H₂S, alkyl mercaptans, carbon disulphide, carbon oxysulphide, alkyl sulphides and alkyl disulphides.¹⁻³ Many of these species can present challenges for producers as they are required to be removed.⁴⁻⁷ H₂S is the most commonly encountered and troublesome contaminant and is responsible for corrosion in the oil and gas industry as well as the well-known health and safety concerns of this very toxic gas.^{1,8} Often overlooked and over-shadowed by H₂S, are the alkyl mercaptans which also need to be removed to reduce the overall undesirable volatile sulphur content of the produced fluids and gases.

Whilst not as hazardous as H₂S, mercaptans do bring about unwanted challenges. They are responsible for the occurrence of foul odours which are especially noticeable in produced waters and create a negative environmental impact.⁹ Mercaptans have been reported to exacerbate high temperature corrosion in crude and condensate distillation units.¹⁰ Mercaptans are also well known to reduce the fiscal value of gas and crude oil if present in sufficiently high concentrations.¹¹

1
2
3 Conventional chemical H₂S scavengers, especially triazine based species, are widely thought to also
4 scavenge alkyl mercaptans, but to a lower degree of efficiency.^{12,13} There is sparse literature on the topic
5 of chemical mercaptan scavenging and even less on structure-activity relationships and mechanisms of
6 scavenging. Two studies stand out; the first reported individual chemical scavengers evaluated against
7 H₂S and methanethiol (or methyl mercaptan) gas mixtures using conventional gas breakthrough as a
8 measure of scavenging efficiency.^{13,14} The analysis of methyl mercaptan in the presence of H₂S was
9 achieved using a sophisticated UV/VIS method (ranging from 200 to 800 nm) in which the absorbance for
10 each sulphur containing species was mathematically isolated. A series of proprietary undisclosed
11 scavengers were tested against conventional triazine and glyoxal based benchmark products. It was found
12 that one formulation was superior to all other tested. While this study did evaluate methyl mercaptan
13 and H₂S in the same gas feed, no higher mercaptans were evaluated. This left open the question of the
14 structure activity relationship for larger mercaptans, as well as giving little detail on the chemistry or
15 mechanisms of action. The second detailed work studied a gas contact tower application for scavenging
16 methyl, ethyl and propyl mercaptan using a variation of the steady state gas breakthrough test to measure
17 the efficiency of various chemistries.¹² The assay was a sulphur specific flame ionisation detector in a gas
18 chromatogram and showed that scavenging mercaptans using known benchmarks for H₂S scavenging, was
19 less efficient. It was suggested that the lower observed efficiencies were due to the higher pKa (lower
20 acidity) of mercaptans relative to H₂S. Most importantly, this study also postulated the first part of the
21 reaction of mercaptans with hexahydrotriazine, however the researchers were not able to isolate and
22 identify the proposed structures.
23
24
25
26
27

28 Several field performance studies are readily available in the open literature however many lack concrete
29 chemical data and mechanistic understanding cannot be derived from these studies. Some studies are
30 noteworthy however, as one can build up an empirical picture from them. For instance, a hydrocarbon
31 condensate /produced water separation tank was treated for mercaptan removal.¹⁵ In this multiphase
32 application a mercaptan scavenger (undisclosed chemistry) identified from lab studies was successfully
33 applied over a period of 7 days and it was found that 300 ppm of scavenger successfully reduced the heavy
34 mercaptan fluid level from ~500 to 600 ppm down to an acceptable 20 ppm. The primary driver for this
35 case history was to reduce the offensive odours for which the mercaptan was responsible. Unfortunately,
36 no details of the chemistry used were provided. In another field-based study acrolein was used to
37 scavenge mercaptans and a generic mechanism was proposed.¹⁶ Undisclosed mixtures of (simple) amines
38 have also been reported in the HYSWEET[®] process for both H₂S and mercaptans, but again no mechanistic
39 details were proposed.^{17,18} A novel oxidation process was reported to treat stored natural gas already
40 treated with odourants (tert-butyl mercaptan and dimethyl sulfide) that utilized a combination of
41 hydrogen peroxide and caustic.¹⁹ This is not the only proprietary oxidative processes reported in the
42 literature and other studies specifically report methyl mercaptan and ethyl mercaptan removal using
43 various hardware.^{20,21}
44
45
46
47

48 What is clear from the previous studies is that it is certainly possible to scavenge mercaptans with
49 common H₂S scavengers but, in order to develop better products and optimize treatment dosages, an
50 improved understanding of the mechanism involved must be developed. This paper contributes to this
51 understanding by presenting a synthesis of our experimental findings on the scavenging of mercaptans
52 using multiple chemical means. In addition, our conjectured mechanisms focusing on the two most
53 common scavengers used today in the industry, viz. 1,3,5-trimethylhexahydro-s-triazine (MMA-Triazine)
54 and 1,3,5-tris(2-hydroxyethyl)hexahydro-s-triazine (MEA-Triazine).
55
56
57
58
59
60

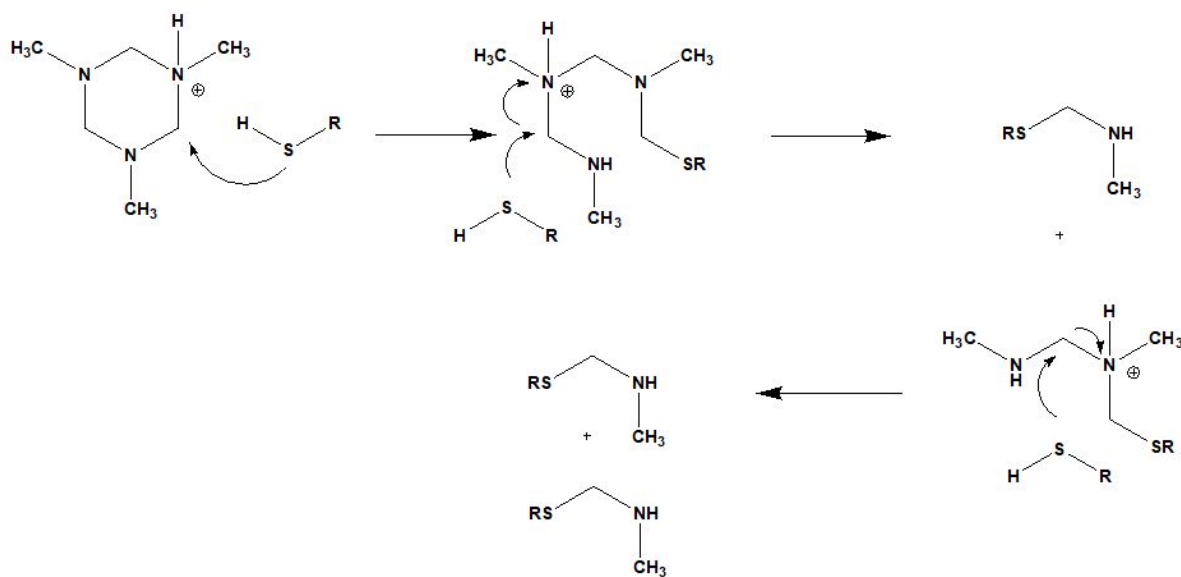
1
2
3 In the current study, for the first-time numerical values for the capacity of various prominent scavengers
4 and their reaction with volatile alkyl mercaptans have been determined and compared directly with the
5 corresponding values for H₂S under identical reaction conditions. Furthermore, the chemical structures of
6 the reaction byproducts with alkyl mercaptans, to date only suggested but neither measured nor
7 confirmed, have been proven by the application of rigorous analytical methods.
8
9

10 11 12 **Reaction Mechanism of Alkyl Mercaptans with Triazine Species: Current Understanding**

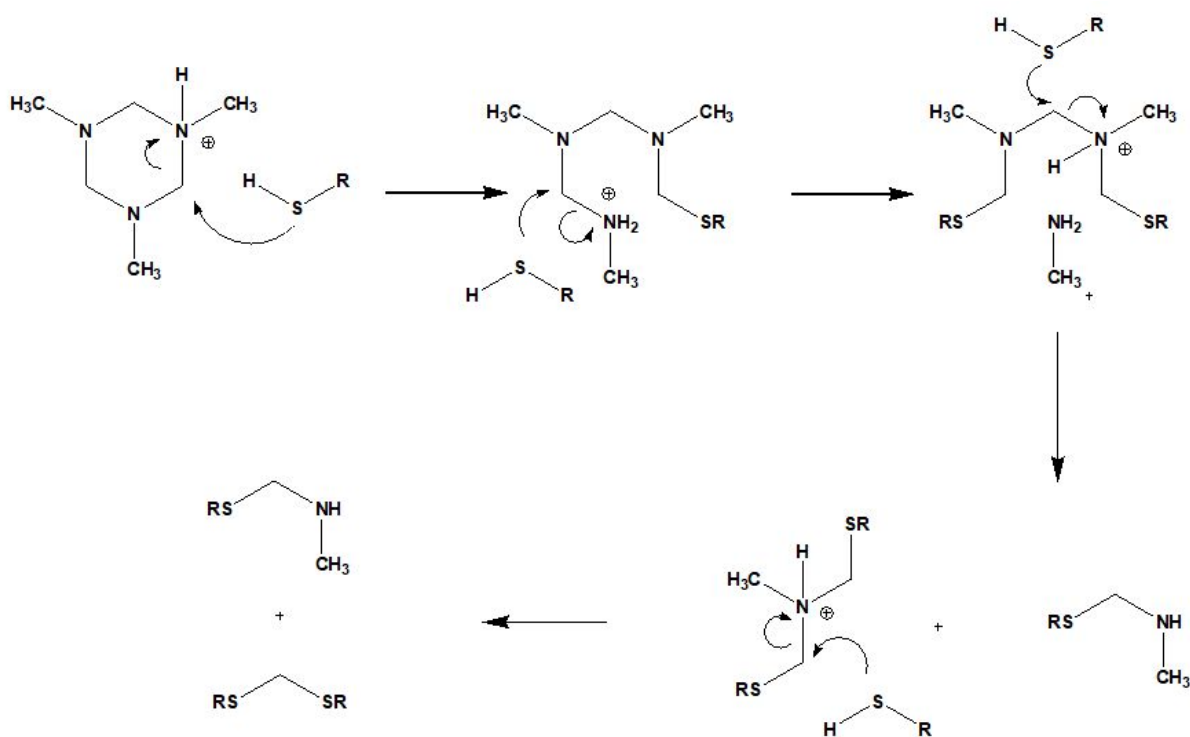
13 The well understood reaction mechanism of H₂S with triazine species is taken as a basis for understanding
14 the corresponding mercaptans reaction.^{22,23} As an example, we shall focus on MMA-triazine. The general
15 reaction of all triazine species with H₂S can be summarized as a sequential nitrogen displacement by the
16 sulphur species. In order to achieve this while maintaining the cyclic structure, each molecule of H₂S
17 undergoes a double S_N2 reaction and thereby eliminates the original amine from which it was derived.²⁴
18 Despite some notions to the contrary, the reaction stops at only two sulphur insertions yielding the
19 ultimate byproduct, 5-(2-hydroxyethyl) hexahydro-1,3,5-dithiazine (dithiazine). This either remains as a
20 monomeric (and sometimes crystalline) material or it can undergo a further polymeric reaction to form
21 the well-known solid fouling, amorphous polymeric dithiazine (apDTZ). It is this latter material that has
22 often been mistaken for the three sulphur cyclic species, 1,3,5-trithiane, a species which has never been
23 isolated during a reaction of triazine with H₂S.
24
25
26

27 Due to the presence of a carbon-sulfur bond, alkyl mercaptans cannot undergo the same double S_N2 type
28 reaction but are confined to only a single S_N2 reaction. This restriction precludes immediately the
29 possibility of cyclic byproducts. The most logical reaction mechanism is therefore shown in Figure 1 which
30 has only been suggested in part but has to date remained unverified by structural analysis.¹² In this
31 reaction, the mercaptan nucleophilicity opens the ring of the triazine but the pendant thioalkyl group
32 cannot close the ring again without the formation of an unlikely sulphonium species. Instead the acyclic
33 byproduct, which still retains all three nitrogen atoms, is proposed to be the initially formed reaction
34 product (I). Successive alkyl mercaptan molecules can further attack the nucleophilic carbons and at each
35 point eliminate a single nitrogen species (II).
36
37
38

39 In fact, there is a second possible pathway for the reaction to proceed once the initial ring fracture has
40 occurred and is described by Mechanism B, shown in Figure 2, where the second alkyl mercaptan residue
41 remains with the two-nitrogen species (III) and eliminates the primary amine (for example methylamine).
42 In the latter mechanism, there are two byproducts that each contain two sulphur atoms, (III) and (IV), in
43 the former there are none. It is unclear from theoretical considerations which of these two mechanisms
44 would be preferred or whether both do in fact take place. (IV) would not be expected to undergo a further
45 nucleophilic attack, since this carbon center is flanked by a nitrogen and a sulphur atom. By the same
46 argument, triazines do not form the three-sulphur species 1,3,5-trithiane during the reaction with H₂S.
47
48
49
50
51
52
53
54
55
56
57
58
59
60



24 **Figure 1 – Mechanism A: The most logical mechanism for reaction of alkyl mercaptans**
25 **with MMA-triazine (R = alkyl)**



54 **Figure 2 – Mechanism B: Alternative reaction mechanism for the reaction of alkyl mercaptan with**
55 **MMA-triazine (R = alkyl)**

1
2
3 One immediate observation common to both mechanisms is the increase in reaction stoichiometry from
4 2 (practical) moles of H₂S per mole of triazine to 3 moles of alkyl mercaptan. This is contrary to the industry
5 perception for these scavengers, which is that they are worse for mercaptan scavenging. Noteworthy
6 however is that whilst the theoretical stoichiometry for the reaction of H₂S with triazine is 4 moles of H₂S
7 to every mole of triazine, the 2 molar equivalents resulting from the salting of the released amine with
8 H₂S is usually disregarded on the assumption that any acid gas can consume this capacity and very likely
9 carbon dioxide would predominate and therefore practical application result in a closer to two moles of
10 H₂S per mole of triazine. The inability of triazines to form 1,3,5-trithiane with H₂S is now overcome via a
11 different reaction pathway and this inevitably leads to a question regarding the popular hypothesis that
12 mercaptans react with triazine but less efficiently than with H₂S. In fact, the above considerations would
13 tend to suggest the reverse.
14
15
16
17
18

19 **EXPERIMENTAL**

20 **Measurement of Mercaptan Scavenging Efficacy Using Common H₂S Scavengers**

21
22 The uptake capacity of a series of conventional H₂S scavenger chemistries for alkyl mercaptans and H₂S
23 were measured directly. The protocol chosen was the elegant and widely used multiphase autoclave
24 method.²⁵ Figure 3 shows a schematic of the type of autoclave set up and sulfur-species analyser used in
25 this study. The method relies on the dissolution of sulfur species in the feed gas into a specified liquid
26 medium in the autoclave. In this study custom gas blends were used that contained 3,000 ppm of sulfur
27 species (either H₂S, methyl or ethyl mercaptan) and 6,000 ppm CO₂, balanced with nitrogen. The liquid
28 medium in the autoclave can be hydrocarbon, brine or a mixture of the two; here, equal volumes of
29 kerosene (as the hydrocarbon phase) and NACE standard brine (as the aqueous phase) were used. After
30 insertion of the fluid into the autoclave, the system is brought up to temperature and pressure (in each
31 case 70°C and 300 psi was used) and the purge gas is passed through the medium at a carefully controlled
32 600 mL.min⁻¹. After an equilibration period the fluid is fully saturated and the concentration of sulphur
33 species in the outflow gas is measured at the same concentration as the inflow gas (i.e. the expected 3,000
34 ppm) and a steady state has been established. At this point, a specified aliquot of scavenger is injected
35 through a pressurized flow loop and a resulting perturbation in the steady state of sulfur species detection
36 is observed and measured as the system returns to equilibrium. The size and profile of this perturbation
37 in the sulfur species enables a calculation of the mass (in micromoles) of sulphur species removed, i.e. the
38 scavenger capacity, given that the volume of scavenger injected is known. The slope of the initial reduction
39 of sulfur species gives an empirical indication of the kinetics of the reaction.
40
41
42
43
44

45 Using this methodology, a series of 6 common oilfield scavengers were evaluated for their ability to
46 scavenge H₂S, methyl mercaptan and ethyl mercaptan and the results from these experiments are
47 presented in Tables 1, 2 and 3, respectively.
48
49
50
51
52
53
54
55
56
57
58
59
60

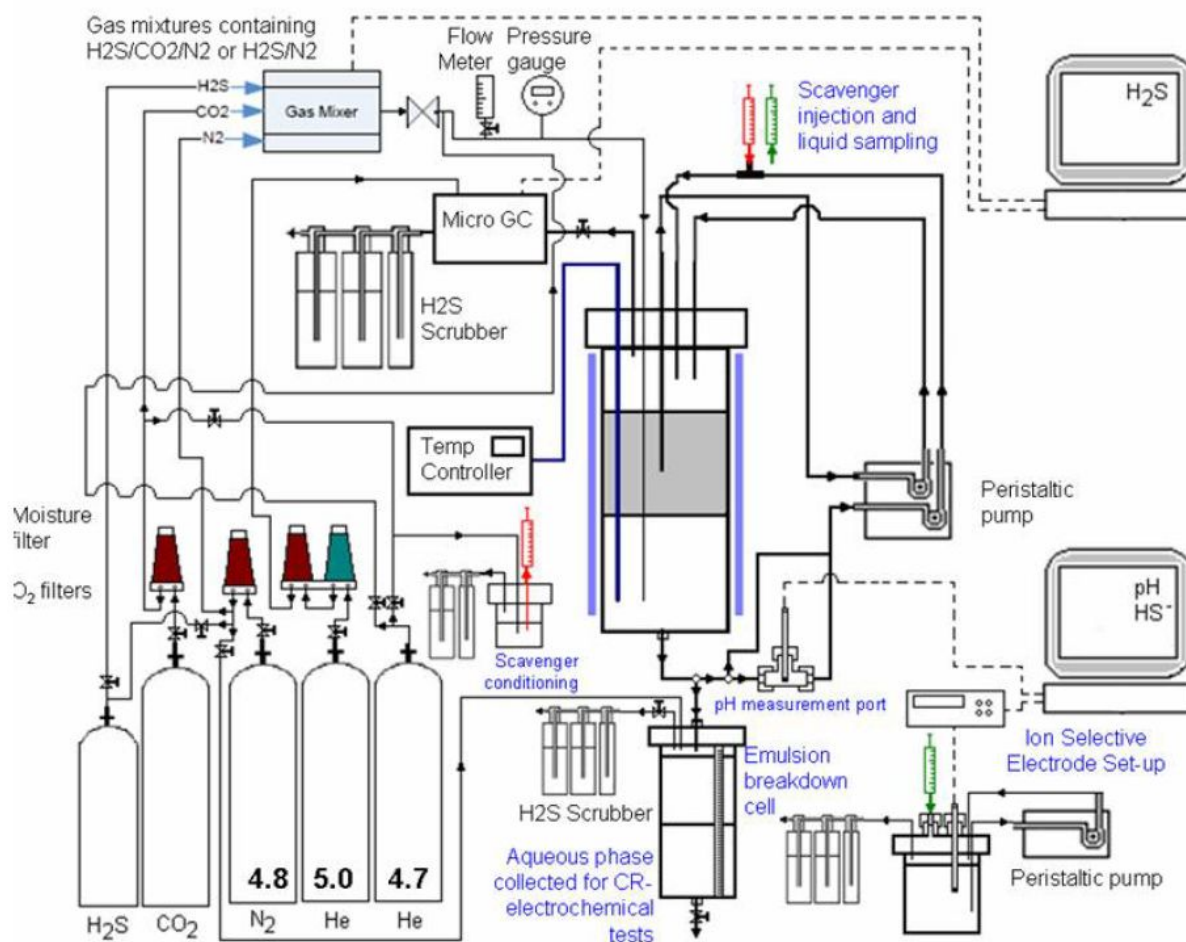


Figure 3 – Schematic of the autoclave technique originally developed and previously reported and used as a design basis for the autoclave used in the current study²⁵

Table 1 – Common scavenger capacities for H₂S as measured by the autoclave method

Scavenger Common Name	Scavenger IUPAC Name	Activity (%)	Experimental capacity (kg H ₂ S.L ⁻¹)	Theoretical capacity (kg H ₂ S.L ⁻¹)	Assumed stoichiometry	Efficiency (%)
MEA-Triazine	1,3,5-tris(2-hydroxyethyl) hexahydro-s-triazine	38	0.12	0.13	2	96.0
MMA-Triazine	1,3,5-trimethylhexahydro-triazine	40	0.23	0.25	2	101.8
Glyoxal	Ethandial	40	0.15	0.19	3/2	76.3
Zinc carboxylate	Zinc-2-ethylhexanoate	18 (as zinc)	0.05	0.11	1	42.9
Synergized hemiformal	Complex alcohol hemiformal oligomer mixture	17 (as HCHO)	0.15	0.21	1	68.7
Unsynergized hemiformal	Complex alcohol hemiformal oligomer mixture	38 (as HCHO)	0.22	0.47	1	45.4

Table 2 – Common scavenger capacities for methyl mercaptan as measured by the autoclave method

Scavenger Common Name	Scavenger IUPAC Name	Activity (%)	Experimental capacity (kg H ₂ S.L ⁻¹)	Theoretical capacity (kg H ₂ S.L ⁻¹)	Assumed stoichiometry	Efficiency (%)
MEA-Triazine	1,3,5-tris(2-hydroxyethyl) hexahydro-s-triazine	38	0.14	0.27	2	52.2
MMA-Triazine	1,3,5-trimethylhexahydro-triazine	40	0.47	0.48	2	98.1
Glyoxal	Ethandial	40	0.25	0.26	∞	95.4
Zinc carboxylate	Zinc-2-ethylhexanoate	18 (as zinc)	0.21	0.16	1	131.3
Synergized hemiformal	Complex alcohol hemiformal oligomer mixture	17 (as HCHO)	0.34	0.30	1	111.1
Unsynergized hemiformal	Complex alcohol hemiformal oligomer mixture	38 (as HCHO)	0.34	0.67	1	58.6

Table 3 – Common scavenger capacities for ethyl mercaptan as measured by the autoclave method

Scavenger Common Name	Scavenger IUPAC Name	Activity (%)	Experimental capacity (kg H ₂ S.L ⁻¹)	Theoretical capacity (kg H ₂ S.L ⁻¹)	Assumed stoichiometry	Efficiency (%)
MEA-Triazine	1,3,5-tris(2-hydroxyethyl) hexahydro-s-triazine	38	0.29	0.35	2	82.9
MMA-Triazine	1,3,5-trimethylhexahydro-triazine	40	0.53	0.62	2	85.5
Glyoxal	Ethandial	40	0.00	0.34	∞	0.9
Zinc carboxylate	Zinc-2-ethylhexanoate	18 (as zinc)	0.17	0.20	1	83.3
Synergized hemiformal	Complex alcohol hemiformal oligomer mixture	17 (as HCHO)	0.16	0.39	1	40.5
Unsynergized hemiformal	Complex alcohol hemiformal oligomer mixture	38 (as HCHO)	0.45	0.86	1	60.0

The experimental results are quite surprising since they are contrary to the widely held “industry perception” that H₂S scavengers are functional but less effective for alkyl mercaptan species. In summary, although the results show some scatter, the overall trend is clear: H₂S scavengers are effective against methyl and ethyl mercaptan. In fact, their performance is far better than the industry consensus. The most effective scavenger from these multiphase results is MMA-triazine, a very under-utilized scavenger when compared and to the almost ubiquitous industrial use of MEA-triazine by the oil and gas industry.¹

When scrutinizing the results, MEA-triazine gave very good scavenging capacities for H₂S and ethyl mercaptan but performed less well at scavenging methyl mercaptan. The explanation of this observation is somewhat unclear especially given that MMA-triazine gave an excellent scavenging capacity for all three sulphur species tested. When comparing the absolute capacity in kg L⁻¹ it must be considered that the sulphur species have significantly different molecular weights. The efficiency or comparison to the theoretical value is the best parameter to use for scavenging performance assessment.

Glyoxal is also a good scavenger for H₂S and methyl mercaptan but its performance dropped off markedly to negligible levels when used scavenging ethyl mercaptan. Previous studies have shown similar

1
2
3 observations and there is an expected structure activity relationship in which heavier mercaptans would
4 be scavenged less efficiently due to steric hindrance effects.¹³
5

6 Zinc carboxylate is an excellent scavenger overall and exceeded the theoretical performance estimate in
7 the case of H₂S. This result does bring into question the assumed stoichiometry, although it is indeed
8 possible that it exceeds the assumed 1:1 allowing multiple sulfur species molecules to be included within
9 the structural matrix. More work is required to fully understand this complex reaction mechanism with
10 scant literature being available which addresses this topic.²⁶
11
12

13 Hemiformal or formaldehyde releaser scavengers show reasonably good performance against mercaptans
14 but with some degree of scatter in the results. The products used have been described in previous work
15 by the current authors.²⁷ On average one would expect a performance optimized (i.e. specifically
16 formulated) or synergized hemiformal to perform the best and this is observed in the case of H₂S and
17 methyl mercaptan. However, the synergized hemiformal, has a lower activity of available formaldehyde.
18 It is possible that there is some threshold effect in the case of less reactive mercaptans that puts
19 hemiformals with a higher level of formaldehyde at an advantage even although they may not be
20 optimised by the synergist. Further it should be considered that the synergist present was developed for
21 reaction with H₂S and may not be effective for reactions with mercaptans. More investigation would be
22 required to confirm this aspect of the results.
23
24

25
26 Noteworthy is a further test performed on methyl mercaptan but not reported in Table 2 along with the
27 rest of the commercial scavenger chemistries. This test concerned tetra-n-butyl ammonium hydroxide.
28 This species is reported as a useful mercaptan scavenger and was chosen as an example of the proposed
29 mercaptan scavenging capacity of ammonium quats *via* an alkyl transfer type reaction to form a
30 sulphonium salt as shown in Figure 4.²⁸ In this study tetra-n-butyl ammonium hydroxide was run as a
31 potential scavenger in an autoclave test with methyl mercaptan. During this test run there was no change
32 to the steady state observed at all after injection indicating zero methyl mercaptan was consumed by the
33 quaternary hydroxide under these conditions.
34
35

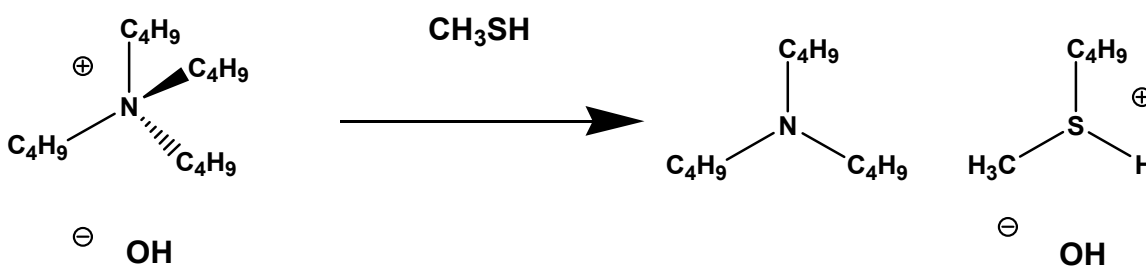


Figure 4 – Proposed reaction of tetra-n-butyl ammonium hydroxide with methyl mercaptan

Measurement of Mercaptan Scavenging Reaction Kinetics Using Common H₂S Scavengers

The data obtained from the autoclave test method described previously is based on the perturbation from an otherwise steady state situation. Integration of the curve from steady state gives an accurate measure of the total sulphur species consumed by the volume of scavenger injected, and thus a capacity (kg RSH per liter) can be calculated. A relative measure of the reaction kinetics can also be obtained by calculating the initial decrease in detected sulphur species and the linear slope of this trendline can yield a relative reaction rate in parts per million of sulphur species (i.e. H₂S or alkyl mercaptan) per minute.

In all cases shown in Tables 1, 2 and 3, each initial linear decrease in detected sulphur species immediately after introduction of the scavenger chemical was extracted from the data set, a trendline was created and a linear equation derived. In each case the slope was taken as a relative measure of reaction kinetics between the scavenger and the various sulphide species. It is understood that this value is not a formal kinetic rate constant (k), rather it is to be regarded as a relative reaction rate expression that enables the kinetic behaviour of the scavengers tested to be compared. This calculated reaction rate has been summarized for all tests in Figure 5.

Several interesting points on these scavenging reactions emerge from this data set. Firstly, for all chemistries tested, the rate of scavenging for each individual species is better the lower the molecular weight of the sulphur species, except for the 2 triazines. From the data in Figure 5, both triazine species tested were excellent scavengers for both alkyl mercaptans, although in both cases the reaction rate drops of markedly in the progression from methyl to ethyl mercaptan. The triazines in this study reacted faster with methyl mercaptan than H₂S which, based on the conventional view was very surprising. Glyoxal is not a good choice for scavenging alkyl mercaptan, and zinc carboxylate also shows rather performance. Both versions of the hemiformal, or formaldehyde releasers, are good in their reaction rates but fall off sharply with ethyl mercaptan. Surprisingly, it was the *unsynergised* hemiformal scavenger that gave the better reaction rate when compared to the synergized hemiformal. This was unexpected as the synergist was developed to render the hemiformal species kinetically able to scavenge H₂S out of a gas stream in a tower application.²⁹ Autoclave testing evaluates a scavenger in a multiphase environment and the interesting observation is that formulations can be specific for application types.

In summary, it is once again MMA-triazine that appears to have the best overall scavenger reaction rate for the two mercaptan species tested and is consistent with the capacity data. Much more work would be required to properly quantify the reaction kinetics of these species and some good studies are available in the literature for MEA-triazine.³⁰

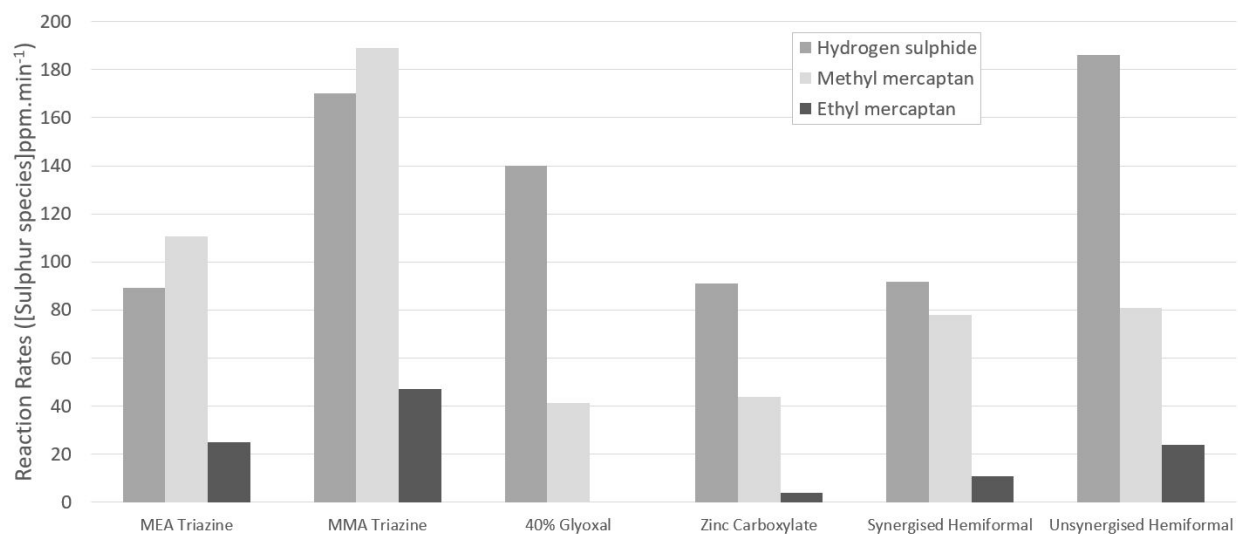


Figure 5 – Common scavenger reaction kinetics for H₂S, methyl mercaptan and ethyl mercaptan as measured by the autoclave method

Investigation of Methyl Mercaptan and Ethyl Mercaptan MMA-Triazine Scavenger Byproducts

There is a literature gap on the structural elucidation of the reaction product between triazines and alkyl mercaptans, and this is of major importance to this study. Two dilute solutions of MMA-triazine (10 mL of a 1% by mass) were exposed to a continuous gas sparge of 3,000 ppm methyl and ethyl mercaptan (separately) in a small gas contact tower. Enough gas was passed through the fluid to consume 50% of the molar capacity of the MMA-triazine based upon a 3:1 assumed stoichiometry. The spent solution was then continuously extracted with methylene chloride for 6 hours, the organic layer concentrated to small volume and examined by GCMS analysis. Unfortunately, in the MMA-triazine and methyl mercaptan experiment, there were no detectable or assignable peaks identified from the GCMS analysis. MMA-triazine needed no derivatization for optimum GCMS and the ethyl mercaptan reaction gave satisfactory results. The total ion chromatogram of the reaction of MMA-triazine with ethyl mercaptan is shown in Figure 6 and inset is the mass spectrum of the major reaction product component at $R_t = 4.38$ mins.

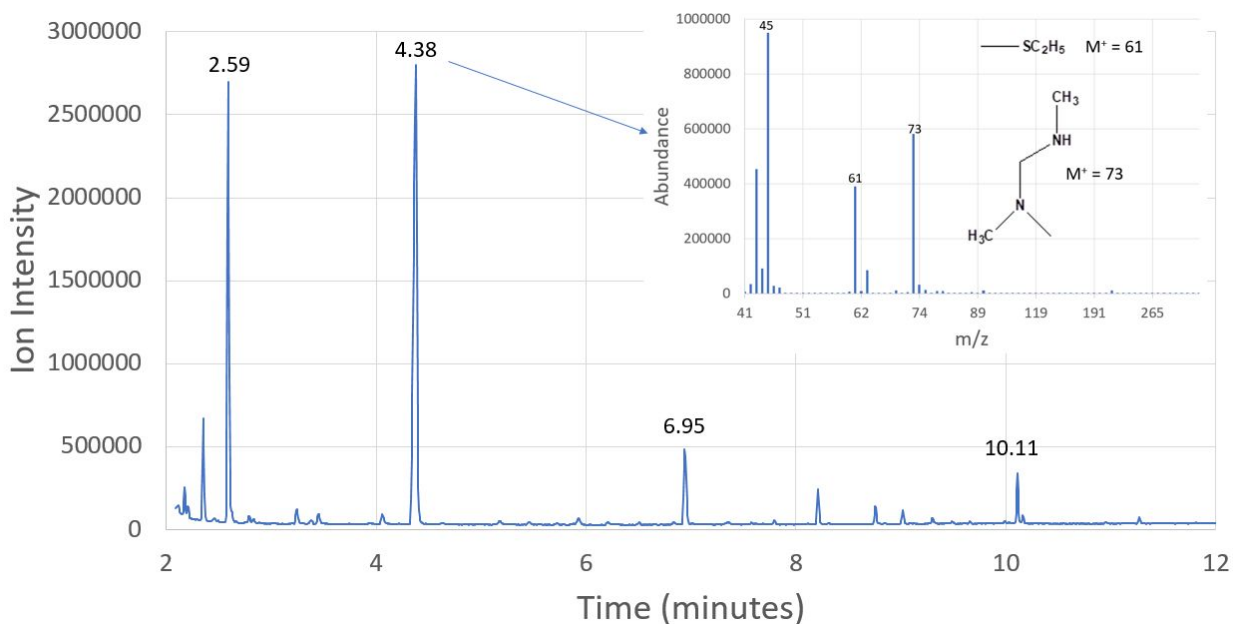


Figure 6 – Total ion chromatogram for MMA-triazine reaction product with ethyl mercaptan and inset mass spectrum on $R_t = 4.38$ min component

There are two very clear fragments at 61 and 73 AMU (Atomic Mass Units) which strongly indicate the suggested mechanism for the reaction shown in Figure 7. The assignment of these two major fragments is also indicated in the reaction products; the ethanethiol fragment (61 AMU) and 1,3-dimethyldiamino-methane (73 AMU) fragments, respectively. This major reaction component is thus assigned to the structure which contains both fragments and can be seen as the two-nitrogen species in Mechanism A shown in Figure 1.

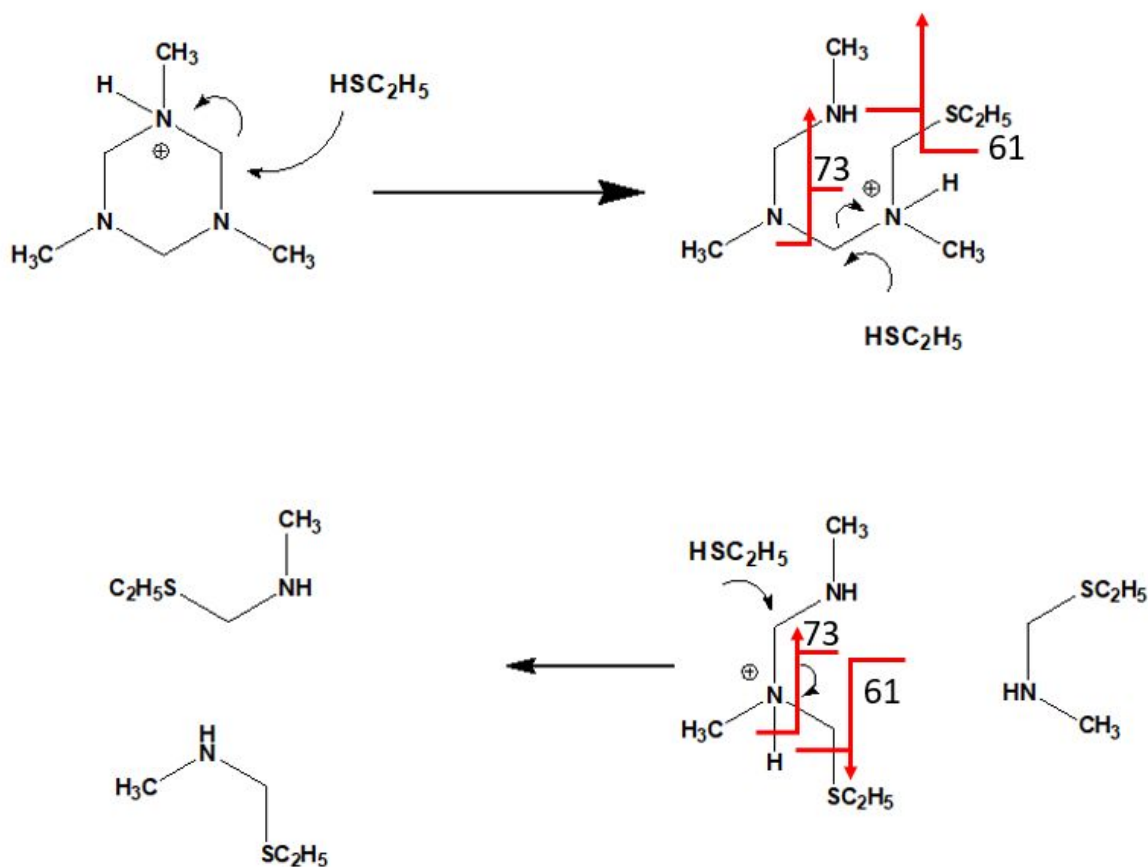


Figure 7 – Proposed reaction mechanism for MMA-triazine and ethyl mercaptan

Investigation of Methyl Mercaptan and Ethyl Mercaptan MEA-Triazine Scavenger Byproducts

As was the case with the experiments with MMA-triazine, a dilute solution of MEA-triazine (10 mL of a 1% by mass) was exposed to a continuous gas sparge of 3,000 ppm methyl and ethyl mercaptan in a small gas contact tower. After the same methylene chloride extraction, GCMS analysis was performed. There were however no assignable peaks detected for either reaction with methyl mercaptan or ethyl mercaptan. It is most likely that the terminal hydroxyl functionalities on the MEA-triazine make it very unsusceptible to successful GCMS analysis, this has previously been observed.²² It is indeed for this reason that the heavier mercaptan species were tested. It is also assumed that the mechanism will be identical for all species of mercaptans from methyl through to butyl.

Investigation of Propyl Mercaptan and Butyl Mercaptan MMA-Triazine Scavenger Byproducts

In the previous experiments with methyl and ethyl mercaptan, very dilute solution could only be formed from the gas phase (3,000 ppm sulfur species). Whilst some encouraging structural information was

determined, it was recognised that the low levels of reaction product could induce some ambiguity caused with such a dilute gaseous mercaptan feed. In order to improve on this information, reactions of the same triazine species were carried out using high concentration (as supplied) liquid mercaptans; viz. 1-propanethiol (propyl mercaptan) and 1-butanethiol (butyl mercaptan) with boiling points of 68°C and 98°C, respectively. Small scale reactions were set up in stirred reaction vials using concentrated aqueous solutions of MMA-triazine (at 40% active) with the molar equivalents of each mercaptan at the expected stoichiometry. Of interest here is the identification of the single-nitrogen molecular species since this would validate the entire chain of reaction. The reactions were stirred at room temperature overnight and the resulting two-phase reaction mixture was partitioned between methylene chloride and water.

In the case of MMA-triazine, both the organic and aqueous layers from the above experiment were analysed via GCMS-Electron Ionization (EI). As expected, the aqueous layer contained the majority of the unreacted triazine. The organic layer contained a small quantity of unreacted triazine together with the identified reaction products as shown in Figure 8 for propyl mercaptan, with the corresponding mass spec identifications at $R_t = 14.20$ inset. In Figure 8, the other components at the various retention times are directly assigned species identifications; notably, and as expected, the alkyl disulphide (di-(n-propyl)-disulphide) was observed and results from the (air) oxidation of propyl mercaptan. The characteristic fragmentation patterns of the mass spectrum at $R_t = 14.20$ minutes shows a molecular fragment at 132 AMU which indicates N-methyl, N-propylthiomethyl-aminomethyl ionic species as shown inset in Figure 8.

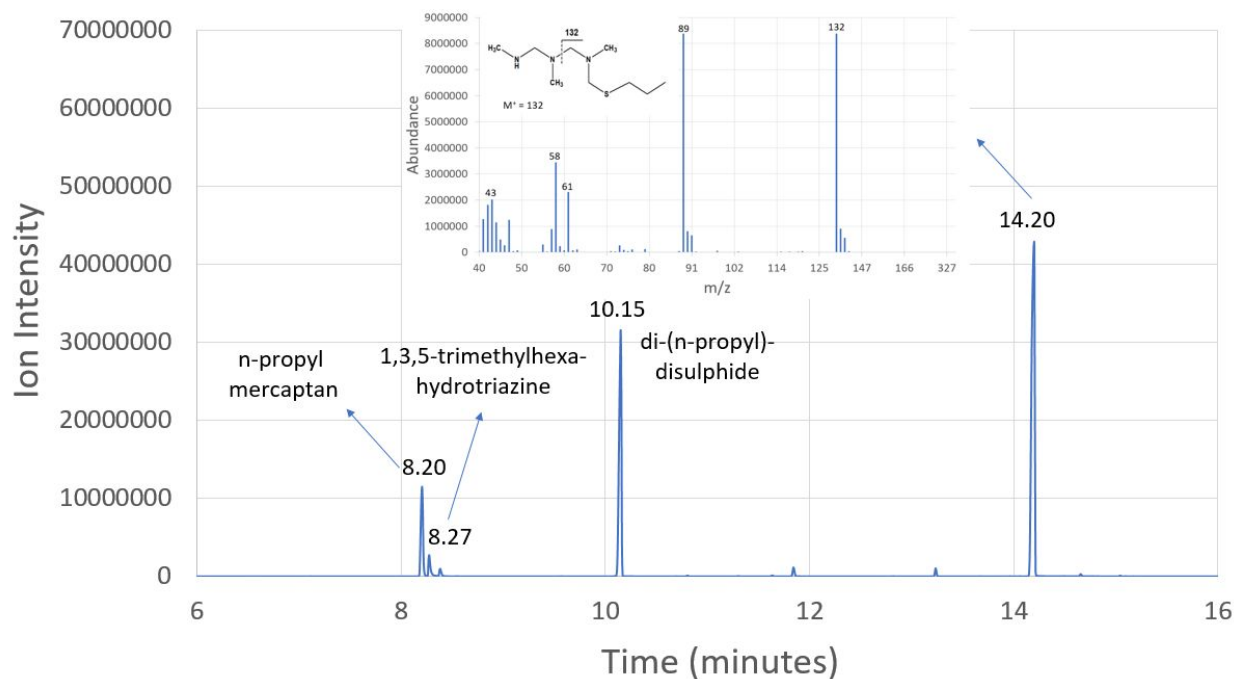


Figure 8 – Total ion chromatogram after reaction of MMA-triazine with propyl mercaptan and inset (top right) mass spectrum of component at $R_t = 14.20$ minutes

The reaction products for butyl mercaptan with MMA-triazine are shown in Figure 9, with the corresponding mass spectrometry identifications at $R_t = 9.67$ and 15.68 minutes inset. Again the other retention times have the other species directly assigned, noteworthy again is the presence of di-(n-butyl)-disulphide resulting from oxidation of butyl mercaptan directly by air. The mass spectrum at $R_t = 9.67$ minutes shows a molecular ion at 133 AMU which indicates an N-methylaminomethyl, butyl sulphide ionic species. Then at $R_t = 14.20$ minutes the molecular fragment at 146 AMU suggesting the N-butylthio-methyl, N-methyl-aminomethyl ionic species.

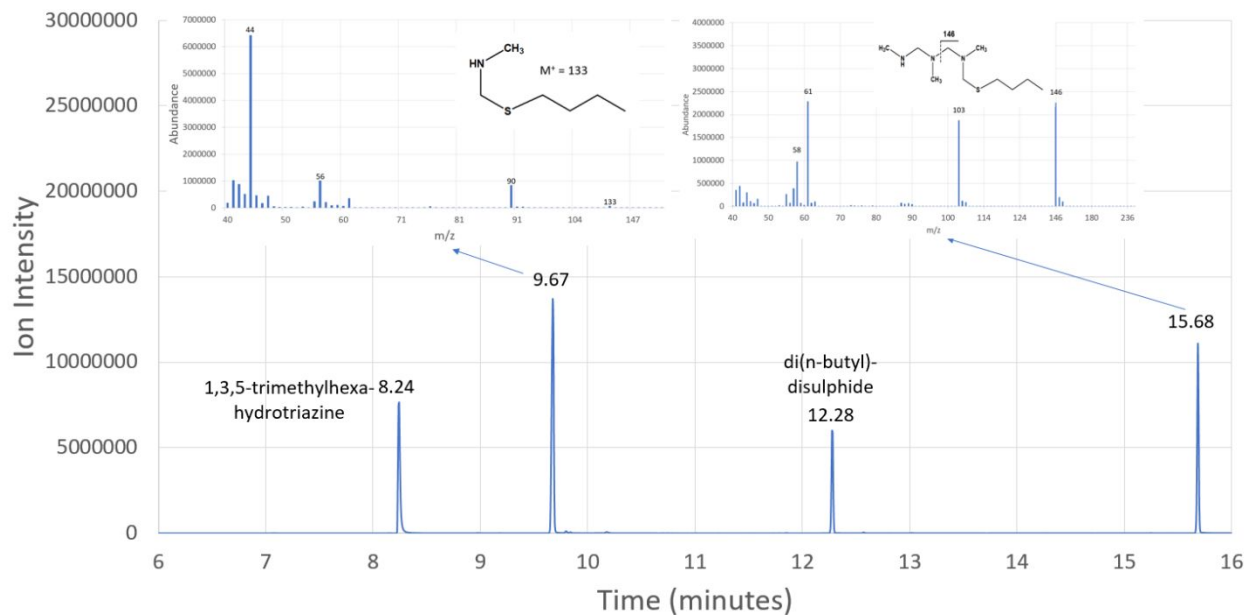


Figure 9 – Total ion chromatogram after reaction of MMA-triazine with butyl mercaptan and inset (top left) mass spectrum of component at $R_t = 9.67$ minutes and (top right) mass spectrum of component at $R_t = 15.68$ minutes

Investigation of Propyl Mercaptan and Butyl Mercaptan MEA-Triazine Scavenger Byproducts

The reaction of heavy mercaptans with MEA-triazine was also carried out using the same procedure as described for experiments with MMA-triazine. However, in this case the two-phase reaction mixtures obtained were not analysed directly. It was thought highly likely that the hydroxyethyl substituents would confer a high level of water solubility on the expected byproducts which would not only partition significantly into the water phase, but also make them very unamenable to GCMS analysis. For this reason, the reaction products were dissolved in a mixture of methyl chloride and water and the resulting two-phase fluid was introduced into a continuous (heavier than water) solvent extraction system. The water phase was continuously extracted with boiling methylene chloride for 8 hours. The resulting organic extract was reduced in volume by about 90% and an aliquot of this concentrate was treated with excess trifluoroacetic anhydride (TFAA) to convert all hydroxyl and amine functionalities to oxygen and nitrogen trifluoroacetates respectively. The TFAA reaction products were then examined by GCMS-EI.

The reaction products for propyl mercaptan with MEA-triazine are shown in Figure 10, with the corresponding mass spectrometry identifications at $R_t = 12.61$ minutes inset and other retention times have the species directly assigned. Tris-trifluoroacetyl-1,3,4-tris(2-hydroxyethyl)-hexahydro-s-triazine is clearly seen at $R_t = 9.32$ minutes and is readily identified by the 266 AMU fragment as well as the disulfide oxidation product of propyl mercaptan at $R_t = 10.11$ minutes. More importantly, the 1-N molecular species for propyl mercaptan is clearly identified at 341 AMU by the N,O-bistrifluoroacetyl-N-propylthiomethyl,N-(2-hydroxyethyl)amine ionic species.

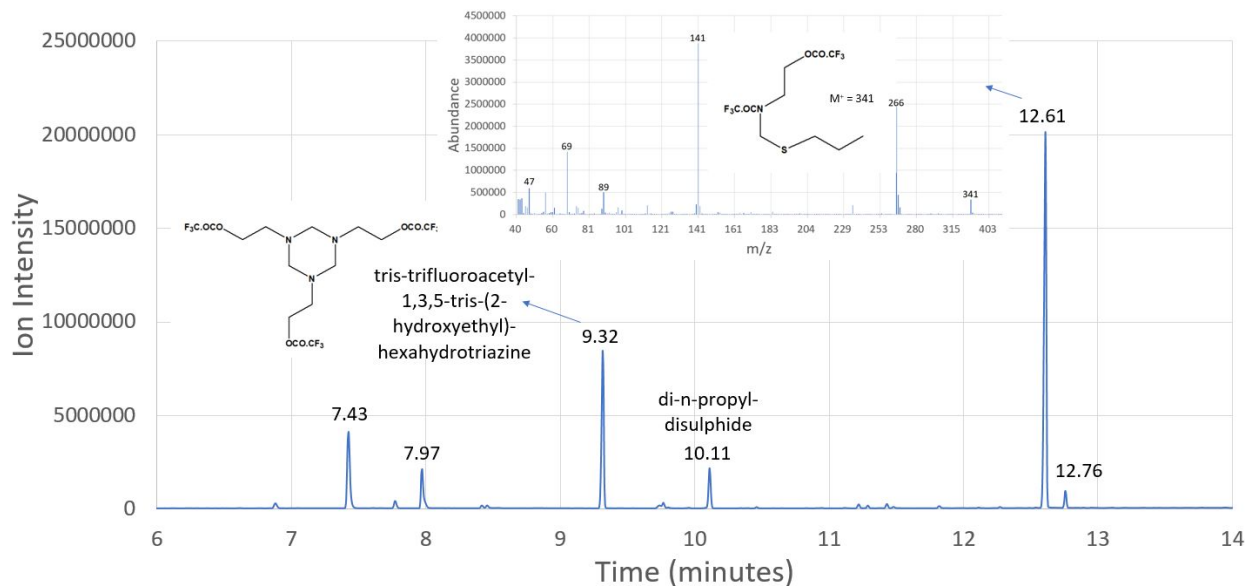
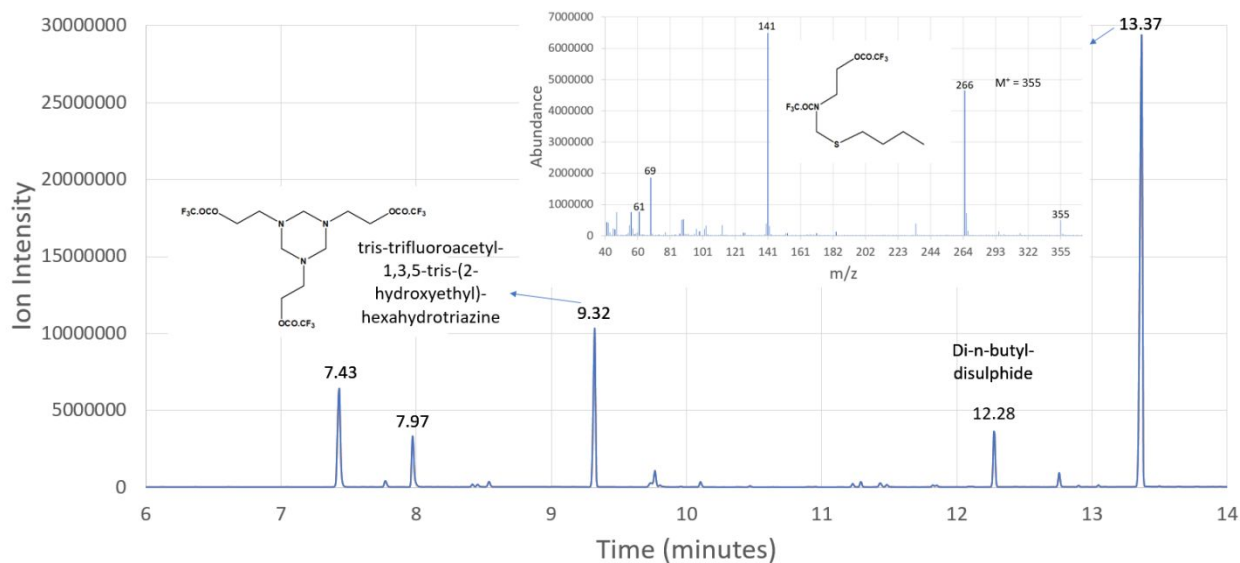


Figure 10: Total ion chromatogram after reaction of MEA-triazine with propyl mercaptan and inset mass spectrum of component at $R_t = 12.61$ minutes



1
2
3 **Figure 11: Total ion chromatogram after reaction of MEA-triazine with butyl mercaptan and inset**
4 **mass spectrum of component at $R_t = 13.37$ minutes**
5
6
7

8 The corresponding reaction products for butyl mercaptan with MEA-triazine are shown in Figure 11, with
9 the related mass spectrometry identifications at $R_t = 13.37$ minutes inset and other retention times have
10 the species directly assigned. The mass spectrum shows a molecular ion 355 AMU which indicates the
11 N,O-bistrifluoroacetyl-N-butylthiomethyl,N-(2-hydroxyethyl)amine ionic species.
12

13 The presence of the molecular species at 341 and 355 AMU for the reactions of propyl and butyl
14 mercaptan (respectively) with MEA-triazine confirms the reaction Mechanism A originally postulated in
15 Figure 1 since it is through this proposed mechanism that the molecule can degrade and sequential
16 nucleophilic substitution of the sulphur nucleophile breaks the molecule down. Larger fragments were
17 not observed in this case (2-N and 3-N species), and this may be due to a complete reaction with the heavy
18 mercaptan and/or the inability of these species withstand the thermal impact of the high injection
19 temperature of the gas chromatography technique.
20
21
22
23

24 **SUMMARY AND CONCLUSIONS**

25 Scavenging of alkyl mercaptans in the oil and gas industry has received much less attention than the much
26 more extensive problem of H_2S scavenging. It has been known for some time that mercaptan scavenging
27 is possible, and indeed as reviewed in this study, some efficacy of conventional H_2S scavengers has been
28 reported in this respect. However, to develop and optimize improved mercaptan scavengers an improved
29 understanding of the mechanism is required. In this paper, we have attempted to contribute to this
30 understanding by presenting a range of experimental findings on the scavenging of mercaptans
31 benchmarked to H_2S . From these results and our analysis of the literature, we test two possible
32 conjectured mechanisms of reaction for triazine species with alkyl mercaptan species – denoted
33 Mechanism A and Mechanism B (as presented in Figures 1 and 2 respectively).
34
35
36
37

38 This current study has, for the first-time, provided a systematic series of quantified scavenging
39 performance results for a variety of prominent scavengers with volatile alkyl mercaptans and directly
40 compared with the corresponding values for H_2S under identical reaction conditions. The scavenging
41 capacity considerations gave some surprisingly good results in that the various conventional H_2S
42 scavengers proved to be much better at scavenging mercaptans than was previously expected. Overall,
43 the best product was found to be MMA-triazine and it is hoped that this observation will further
44 encourage operators to consider using this underutilized triazine candidate in industrial applications
45 where efficient mercaptan scavenging is required.
46
47

48 The chemical structures of the reaction byproducts with alkyl mercaptans, to date only suggested but not
49 previously confirmed, have been proven by the application of rigorous analytical methods. Results for
50 both MMA-triazine and MEA-triazine reactions with ethyl, propyl and butyl mercaptan comprehensively
51 show, via the use of GCMS(-EI) analysis, that it is Mechanism A (Figure 1) that is the most likely scavenging
52 route. Representatives from each step in the sequential reaction pathway, containing each 1, 2 and 3
53 nitrogen atoms have been observed, identified and characterized. Despite a careful search through our
54
55
56
57
58
59
60

spectra, no structures were identified that give any support to Mechanism B, and thus we conclude that Mechanism A is the exclusive and preferred reaction pathway.

AUTHOR INFORMATION

Corresponding Author

J. J. Wylde – Heriot Watt University, Edinburgh EH14 4AS, U.K.; Clariant Corporation, Woodlands, Texas 77381, United States; Email: jonathan.wylde@clariant.com

Authors

G. N. Taylor – Clariant Corporation, Woodlands, Texas 77381, United States

K. S. Sorbie – Heriot Watt University, Edinburgh EH14 4AS, United Kingdom

W. N. Samaniego – Clariant Corporation, Woodlands, Texas, 77381, United States

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

The authors thank Clariant for allowing this work to be published.

REFERENCES

1. Agbroko, O.W., Piler, K. and Benson, T.J. (2017) A Comprehensive Review of H₂S Scavenger Technologies from Oil and Gas Streams. *ChemBioEng Reviews*, **4** (6), 339–359
2. Kohl, A.L and Nielson, R.B. (1997) *Gas Purification*. 5th Edition, Gulf Professional Publishing
3. Kelland, M.A. (2014) Production Chemicals for the Oil and Gas Industry. 2nd Edition, *CRC Press*
4. Silva R.C., Pazinato, M., Marcorighi, J.B., Dias, P. Sampaio, T.P., Bitencourt, J., Hanna, A.W., Paprocki, J., Gomes, M.T., and Rocha, R.B. (2017) Synergistic Combination of Products for Optimization of Oil Well Production and H₂S Reduction. **OTC-28043-MS**. Presented at the *Offshore Technology Conference Brasil, 24-26 October, Rio de Janeiro, Brazil*
5. Dhulipala, P.D.K., Jani, J.K., Wyatt., M.R., Lehrer, S.E., Liu, Z., Leidensdorf, J. and Chakraborty, S. (2018) Bio-Molecular Non-Corrosive Hydrogen Sulfide Scavenger. **SPE-190908-MS**. Presented at *SPE In. Oilfield Corrosion Conf. and Exhib., 18-19 June, Aberdeen, Scotland*
6. Ramachandran, S., Lehrer, S., Chakraborty, S. and Jani, J. (2018) Novel Scavenger Technology for Effective Removal of H₂S from Produced Gas in Oilfield Applications. **SPE-192885-MS**. Presented at the *Abu Dhabi International Petroleum Exhibition and Conference., 12-15 November, Abu Dhabi, UAE*
7. Taylor, G.N., Wylde, J.J., Smith-Gonzalez, M. and Oliveira, A.P. (2019) Recent Breakthrough Advances in the Oil and Gas Industry Search for a Non-Triazine Based Scavenger System in Sulfide

Mitigation: Optimizing the Chemistry and Closing the Gap Between Lab Versus Field Evaluations.
Presented at the 30th TEKNA Oilfield Chemistry Conference, 12-15 March, Geilo, Norway

8. Dhulipala, P.D.K., Wyatt, M.R. and Armstrong, C. (2020) Environmentally Preferable Smart Chemicals for the Oil and Gas Industry. **IPTC-20203-MS**. *International Petroleum Technology Conferences, 13–15 January, Dhahran, Kingdom of Saudi Arabia*
9. Elenbaas, D., Mohamed, B., Khan, M., Hidayati, D., Huang, F. and Lee, R. (1996) The Environmental Impact of Mercaptans in Underground Storage. **SPE-37383-MS**. *Presented at the Society of Petroleum Engineers Eastern Regional Meeting, 23–25 October, Columbus, Ohio, USA*
10. De Jong, J.P., Dowling, N., Sargent, M., Etheridge, A., Saunder-Tack, A. and Fort, W. (2007) Effect of Mercaptans and other organic sulfur species on high temperature corrosion in crude and condensate distillation units. **NACE-07565**. *Presented at CORROSION 2007, 11–15 March, Nashville, Tennessee, USA*
11. Beilby, P.S., Clayton, C. and Moffatt, B.J. (2009) Distribution of Hydrogen Sulfide in the Buzzard Field. **SPE-123875-MS**. *Presented at the Society of Petroleum Engineers Annual Technical Conference and Exhibition, 4–7 October, New Orleans, LA, USA*
12. Owens, T.R. and Clark P.D. (2010) Triazine Chemistry: Removing H₂S and Mercaptans. *ASRL Quarterly Bulletin*, **155**, Vol XLVII, No. 3, 1–21, October-December
13. Chakraborty, S., Lehrer, S. and Ramachandran, S. (2017) Effective Removal of Sour Gases Containing Mercaptans in Oilfield Application. **SPE-184589-MS**. *Presented at the Society of Petroleum Engineers International Conference on Oilfield Chemistry, 3–5 April, Montgomery, Texas, USA*
14. Chakraborty, S., Lehrer, S. and Ramachandran, S. (2017) Effective Removal of Sour Gases Containing Mercaptans in Oilfield Application. **SPE-183974-MS**. *Presented at the Society of Petroleum Engineers Middle East Oil and Gas Show and Conference, 6–9 March, Manama, Kingdom of Bahrain*
15. Passucci, C., Grazioli, G. and Carniani, C. (2009) Innovative Mercaptan Scavengers: First Field Application. **IPTC-13362-MS**. *Presented at the International Petroleum Technology Conference, Doha, Qatar, 7–9 December*
16. Arensdorf, J.J. and Horaska, D.D. (2011) Treatment of Mercaptans in Canadian Condensate. **SPE-141217-MS**. *Presented at the Society of Petroleum Engineers International Symposium on Oilfield Chemistry, 11–13 April, The Woodlands, Texas, USA*
17. Cadours, R., Shah, V. and Weiss, C. (2009) Process for Improved Mercaptan Removal. **IPTC-13512-MS**. *Presented at the International Petroleum Technology Conference, 7–9 December, Doha, Qatar*
18. Cadours, R., Al-Katheeri, S., Al-Mastroushi, M.S., Ghazaly, A. and Sayegh, S. (2015) Mercaptan Removal for Sulphur Emission Mitigation. **SPE-177847-MS**. *Presented at the Society of Petroleum Engineers, Abu Dhabi International Petroleum Exhibition and Conference, 9–12 November, Abu Dhabi, UAE*
19. Sheeran, K., Murray, M., Lehane, J. and O’Flaherty, T. (2012) Oxidation of Mercaptan, Dimethyl Sulfide in Aqueous Waste. **SPE-0212-0028-JPT**. *Journal of Petroleum Technology*, **64** (2), 28–32
20. Mazgarov, A.M. and Vildanov, A.F. (1997) A Selective Treatment of Various Oils and Gas Condensates to Remove Light Mercaptans and Hydrogen Sulfide. **WPC-29271**. *Presented at the 15th World Petroleum Congress, 12–17 October, Beijing, China*
21. Davoudi, M., Khoramdel, I. and Bazregari, B. (2012) Performance Assessment and Optimization of Liquid Petroleum Gas Demercaptanization Process (A Case Study). **SPE-150917-MS**. *Presented at the Society of Petroleum Engineers North Africa Technical Conference and Exhibition, 20–22 February, Cairo, Egypt*

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
22. Taylor, G.N., Prince, P., Matherly, R., Ramakrishna, P., Tompkins, R. and Vaithilingam, P. (2012) Identification of the Molecular Species Responsible for the Initiation of Amorphous Dithiazine Formation in Laboratory Studies of 1,3,5-Tris (hydroxyethyl)-hexahydro-s-triazine as a Hydrogen Sulfide Scavenger. *Ind. Eng. Chem. Res.*, **51**, 11613–11617
23. Matherly, R. and Taylor, G.N. (2013) The Evaluation and Optimization of Hydrogen Sulfide Scavenger Applications Using Ion Mobility Spectrometry. **SPE-164133-MS**. Presented at the SPE International Symposium on Oilfield Chemistry, 8–10 April, The Woodlands, Texas, USA
24. Wylde, J.J., Taylor, G.N., Sorbie, K.S. and Samaniego, W.N. (2020) The Formation, Chemical Characterization and Oxidative Dissolution of Amorphous Polymeric Dithiazine (apDTZ) During the Use of the H₂S Scavenger MEA-Triazine. *Accepted and pending for publication in Energy and Fuels*
25. Mendez, C., Magalhaes, A.A.O., Ferreira, P.A. and Bastos, E.C. (2009) H₂S Scavengers Injection: A Novel Evaluation Protocol to Enhance the Integrity of Production Lines. **OTC 20168**. Presented at the Offshore Technology Conference, Houston TX, 4–7 May
26. Buller, J. and Carpenter, J.F. (2005) H₂S Scavengers for Non-Aqueous Systems. **SPE-93353-MS**. Presented at the Society of Petroleum Engineers International Symposium on Oilfield Chemistry, 2–4 February, Houston, Texas, USA
27. Wylde, J.J., Taylor, G.N., Sorbie, K.S. and Samaniego, W.N. (2020) Synthesis and Reaction Byproduct Characterization and Mechanistic Understanding of Hemiformal Based Hydrogen Sulfide Scavengers. *Energy and Fuels*, **34** (4), 4808–4821
28. Greaney, M.A., Kerby, M.C. and Bearden, R. (2003) Mercaptan Removal from Petroleum Streams (LAW950). **US 2003/0019793 A1**
29. Taylor, G., Smith-Gonzalez, M., Wylde, J.J. and Oliveira, A.P. (2019) H₂S Scavenger Development During the Oil and Gas Industry Search for an MEA Triazine Replacement in Hydrogen Sulfide Mitigation and Enhanced Monitoring Techniques Employed During Their Evaluation. **SPE-193586-MS**. Presented at Society of Petroleum Engineers Oilfield Chemicals Conference, Galveston, Texas, 8–9 April
30. Bakke, J.M., Buhaug, J.B. and Riha, J. (2001) Hydrolysis of 1,3,5-Tris(2-hydroxyethyl)hexahydro-s-triazine and Its Reaction with H₂S. *Journal Ind. Eng. Chem. Res.*, **40** (26), 6051–6054