Preface

The work presented in this dissertation has been executed at the Department of Chemistry, the Norwegian University of Science and Technology in Trondheim, from January 1999 to June 2002. Statoil ASA initiated this work, and I would like to thank them for letting me work on their project. Statoil and the Norwegian Research Council are gratefully acknowledged for their generous financial support.

I would like to express my most sincere gratitude to my supervisor, Professor Jan M. Bakke, for his great enthusiasm and belief in me and my work.

I am deeply grateful to my friends and colleagues at the Department for many hours of small-talk, fruitful discussions and valuable help during my studies. Particularly, I would particularly like to thank siv.ing. Ingrid Sletvold and siv.ing. Bjart Frode Lutnæs for spending hours reading through this thesis. All your comments have been greatly appreciated. Dr.ing. Einar Skarstad Egeland was very helpful in establishing the IUPAC names of many of my compounds, and he is gratefully acknowledged.

Finally, I would like to express my gratitude to my family for the many encouraging phone calls during my many years of education. Lastly, I would like to thank my husband, Halvard, for his love and support, and for colourful ideas for my work.

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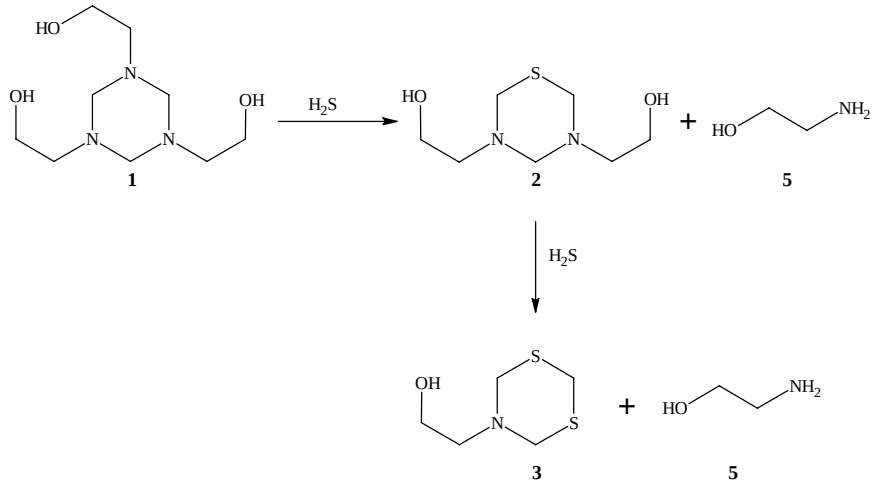
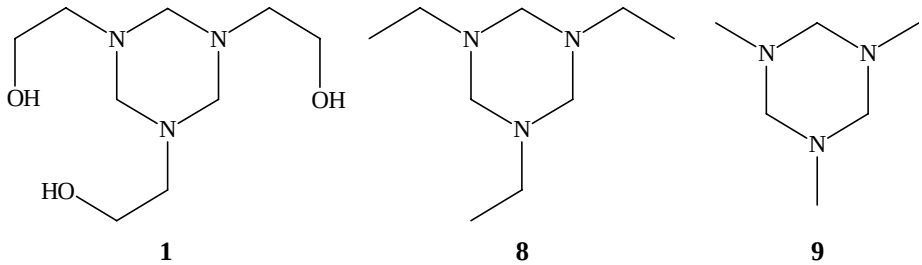
Summary

1,3,5-Tris(2-hydroxyethyl)-1,3,5-triazinane (**1**), in the industry often referred to as "Triazine", is a widely used liquid H_2S scavenger. The goal of the work presented in this dissertation was to examine the chemistry of its reaction with H_2S, and to determine the efficiency of **1** and other potential scavengers in H_2S removal.

It was found that two competing reactions take place when **1** is used as an H_2S scavenger. One is the hydrolysis of the compound, in which ethanolamine (**5**) and formaldehyde is formed. The other reaction is the nucleophilic substitution of sulfur into the triazinane ring. By a combination of various NMR techniques, IR spectroscopy and elemental analysis, the latter reaction was found to proceed as follows:



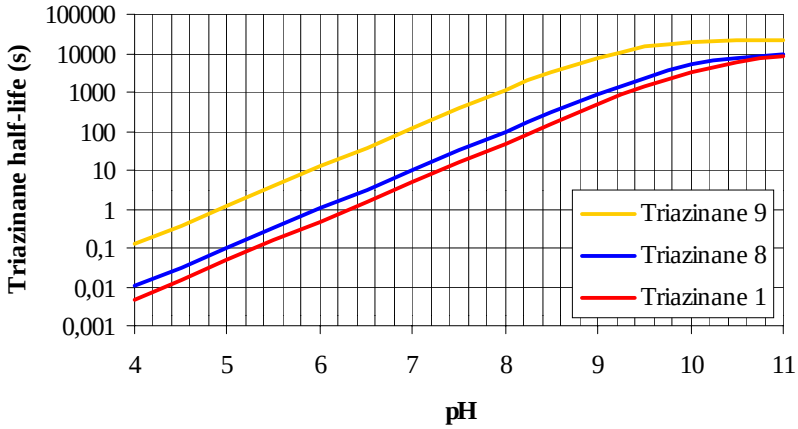
The stability and reactivity of triazinane **1** in H_2S removal was determined by ^1H NMR spectroscopy. The same procedure was used to test the stability and reactivity of two other triazinanes, 1,3,5-triethyl-1,3,5-triazinane (**8**) and 1,3,5-trimethyl-1,3,5-triazinane (**9**).



The hydrolysis of the triazinanes (T) followed the same rate law:

$$-\frac{d[T]}{dt} = k_1[T] + k_2[T][H^+]$$

For each compound, the rate constants k_1 and k_2 were determined, and the half-lives of the compounds were calculated from them.



It was concluded that triazinane (**9**) hydrolysed conciderably slower than the other two compounds. The currently used H_2S scavenger, triazinane **1**, is the least stable of the triazinanes.

Investigations of the reactivity of the three triazinanes with HS^- showed that their reactions followed the same rate law:

$$-\frac{d[T]}{dt} = k[TH^+][HS^-]$$

Triazinane **1**, which is a hydroxyethyl-substituted triazinane, was found to have a higher value for k, and to react considerably faster than the ethyl-substituted (**8**) and methyl-substituted (**9**) triazinanes.

In conclusion, 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane (**1**) was found to be the most efficient of the tested compounds.

Six other potentially H_2S scavenging compounds were examined, but none of them could compete with triazinane **1**, either because the synthesis or analysis of the compound failed, or because no reaction with H_2S was observed.

Symbols & Abbreviations

1D	one-dimensional (NMR)
2D	two-dimensional (NMR)
atm	atmospheres (pressure unit)
Bu	butyl
calcd	calculated
CORR	two-dimensional correlation spectroscopy ($^{13}C,^{1}H$)
COSY	two-dimensional correlation spectroscopy ($^{1}H,^{1}H$)
d	chemical shift in ppm from standard (NMR)
d	doublet (NMR)
DMSO	dimethyl sulfoxide
DNMR	dynamic NMR spectroscopy
e.g.	exempli gratia, for example
EIMS	electron impact mass spectrometry
Et	ethyl
EtOH	hydroxyethyl or ethanol
g	gram
GC	gass chromatography
GC-MS	gass chromatography combined with mass spectrometry
h	hours
HETCOR	heteronuclear correlation spectroscopy ($^{13}C,^{1}H$)
HRMS	high resolution mass spectrometry
Hz	Hertz
IR	infrared
J	coupling constant (NMR)
k	rate constant
k_1	first order rate constant
k_1’	pseudo first order rate constant
k_2	second order rate constant
k_2’	pseudo second order rate constant
k_3’	pseudo third order rate constant
K_a	acid constant
k_{obs}	observed rate constant
M	molar (mol/l)
m	medium absorption (IR)
m	multiplet (NMR)
Me	methyl
MeOH	methanol
MDEA	methyldiethanolamine
MEA	monoethanolamine

MHz	megahertz
min	minute(s)
ml	millilitre(s)
µl	microlitre(s)
mmol	millimole(s)
MS	mass spectrometry
NMR	nuclear magnetic resonance
NOE	nuclear overhauser effect
NOESY	two-dimensional nuclear overhauser effect spectroscopy
pH	negative logarithm of $[H^+]$
pK_a	negative logarithm of K_a
ppm	parts per million
Pr	propyl
q	quartet (NMR)
rel.int.	relative intensity (MS)
rt	room temperature
s	second(s)
s	singlet (NMR)
s	standard deviation (kinetics)
s	strong absorption (IR)
SSE	sum of squares of errors (linear regression)
t	time (kinetics)
T	triazinane (kinetics)
t	triplet (NMR)
$t_{½}$	half-life (time needed to reach half of original concentration)
T_c	coalescence temperature (NMR)
TH^+	triazinane with protonated nitrogen (kinetics)
THF	tetrahydrofurane
TLC	thin layer chromatography
UV	ultra violet
vol%	per cent by volume
w	weak absorption (IR)
wt%	per cent by weight

1 Introduction

The production of natural gas in the North Sea is facing a growing problem: contamination of the natural gas with dihydrogen sulfide, H_2S. As a gas reservoir is emptied, seawater containing sulfates is pumped into it, and the sulfates are reduced to dihydrogen sulfide by sulfate-reducing bacteria. Dihydrogen sulfide is then pumped up along with the oil, gas and water from the reservoir, causing severe corrosion of pipelines and contamination of the final natural gas product. Dihydrogen sulfide is extremely toxic, and in fields with especially large concentrations of H_2S this is a severe health risk for the platform workers. Hence, it is desirable to remove the dihydrogen sulfide at the earliest stage possible.

1.1 H_2S Scavenging

There are four main methods for removing H_2S from natural gas:[1]

- Liquid scavengers
- Solid scavengers
- Liquid redox processes
- Amine / Claus catalyst

Liquid scavengers are widely used in the natural gas industry, especially at sites with relatively low concentrations of H_2S. As a rule of thumb, liquid scavengers are economically favourable at sites with a removal of less than 50 kg/day of H_2S.[1]

Solid scavengers consist mainly of iron-based materials that adsorb H_2S. The hydrogen sulfide can then be desorbed, and the scavenger reused. The solid scavengers are more cost effective than the liquid scavengers when 50-200 kg/day of H_2S is to be removed.[1]

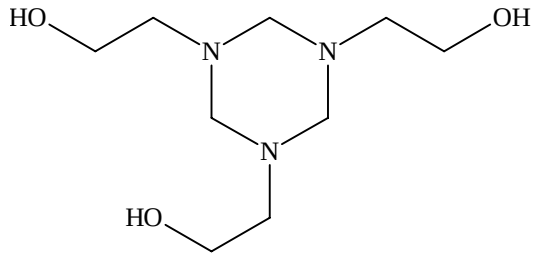
Liquid redox processes are based on the oxidation of H_2S to elemental sulfur, using aqueous solutions containing metal ions. These processes are frequently used when the H_2S removal is between 200 and 2000 kg/day of H_2S.[1]

Amines such as MEA (monoethanolamine) and MDEA (methyl diethanolamine) form complexes with H_2S. When such a complex is treated with a

catalyst, H_2S is oxidized to elemental sulfur. This process if often referred to as a Claus process, and the relatively high cost related to the installation of such a unit makes the process economically unfavourable below 20 tons/day of H_2S removal.[1]

1.2 Liquid Scavengers: "Triazine"

The cyclic amine 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane (**1**), often referred to as "Triazine", is used in fields with relatively low concentrations of H_2S and dominates the liquid scavenger market.[1]



1

Scheme 1.1 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane (1).

When **1** is used as an H_2S scavenger, a 50w% solution of **1** in water is sprayed into the gas stream in what is called a direct injection method. This is done after the natural gas has been separated from the oil and water phases. The products are water-soluble and are removed with the water phase. More than 99.9% of the H_2S is removed from the natural gas in this manner.

Advantages of **1** are the water solubility, caused by the three OH-groups and the nitrogens in the molecule, and the fact that it reacts rapidly and selectively with H_2S. A considerable disadvantage is its susceptibility towards hydrolysis at moderate to low pH. Hence, **1** is expected to be inefficient when added directly into the well, due to low H_2S concentrations and very low pH.

A new and more stable liquid scavenger than **1** would be of great interest to the natural gas industry. In order to achieve this goal, more knowledge about the chemistry involved is essential. This thesis will present the chemical investigation of the role of **1** in H_2S scavenging, using common methods in organic chemistry.

The work presented in this thesis is divided into three parts:

Part I **Qualitative investigations of the reaction between triazinane 1 and H_2S** (Chapters 3, 4 and 5).

Here the analysis of the reaction between **1** and H_2S is examined. The hydrolysis of **1** is investigated in Chapter 3, both qualitatively and quantitatively. The products of the reaction between **1** and sulfide nucleophiles are identified in Chapters 4 and 5.

Part II **Determination of the efficiency of triazinane 1 in H_2S removal** (Chapter 6).

In Chapter 6, a method is developed for determining the efficiency of **1** in H_2S removal, and the reaction kinetics for the reaction between triazinane **1** and HS- is established.

Part III **Suggestion, synthesis and testing of potential new H_2S scavengers** (Chapters 7 and 8).

Using the method developed in Part II, the efficiency of other compounds in H_2S removal was tested. Investigations of other triazinanes are presented in Chapter 7, whereas formaldehyde derivatives, such as trioxanes, tetroxanes and an oxolane, are discussed in Chapter 8.

Relevant theory for this thesis is presented in Chapter 2. All experimental details are given in Chapter 9.

2 Theory

2.1 Dihydrogen Sulfide

Dihydrogen sulfide, H_2S, is a highly toxic and corrosive gas.[2] It is one of the principal compounds involved in the cycle of sulfur in the environment. It occurs naturally in volcanic gases, but it is also produced through bacterial action during the decay of both plant and animal protein. Significant concentrations of H_2S can be found in many natural gas fields due to bacteria-assisted direct reduction of sulfates.

2.1.1 Health Considerations

H_2S is an irritant at low concentrations and causes respiratory problems at higher levels. Extremely high concentrations of H_2S may cause death within minutes. The effects of H_2S exposure at various concentrations in air are presented in Table 2.1.[2]

Table 2.1 Effects of H_2S exposure at various concentrations in air.

Effect	Concentration (ppm)	Duration of exposure
Approximate threshold for odour	0.0005-0.13	< 1 min
Threshold of eye irritation	10.5-21	6-7 h
Acute conjuctivitis (gas eye)	50-100	> 1 h
Loss of sense of smell	150-200	2-15 min
Possible death	> 500	15-60 min

Due to the severe health risk of working with H_2S, the use of the concentrated gas should be minimized. For chemical reactions in aqueous solutions, Na_2S or NaHS may be safer alternatives.

2.1.2 Chemical Properties

Dihydrogen sulfide can undergo a large number of redox reactions, the products of which being sulfur dioxide, sulfate or elemental sulfur.

H_2S has a low solubility in water, only 3.5 g/l H_2O.[3] Na_2S has a solubility of 206 g/l H_2O.[3]

When H_2S is dissolved in water, the following equilibria are established:[3]

$$H_2S + H_2O \rightleftharpoons HS^- + H_3O^+ \qquad pK_{a1} = 7.05$$

$$HS^- + H_2O \rightleftharpoons S^{2-} + H_3O^+ \qquad pK_{a2} = 19$$

Scheme 2.1 Equilibrium of H_2S.

Which protonation state is likely to dominate a solution is given by the equations in Scheme 2.1. The results are given in Figure 2.1:

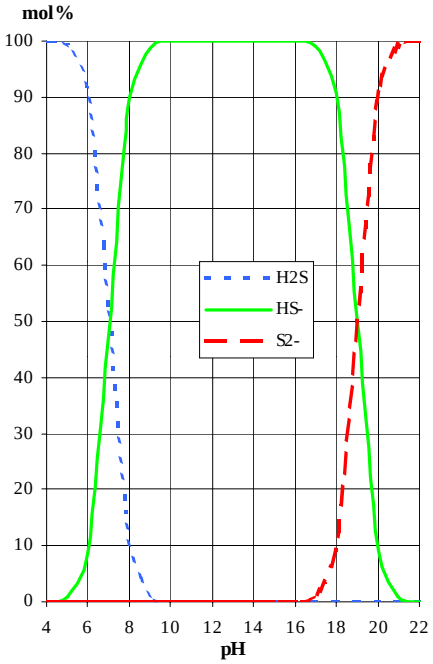


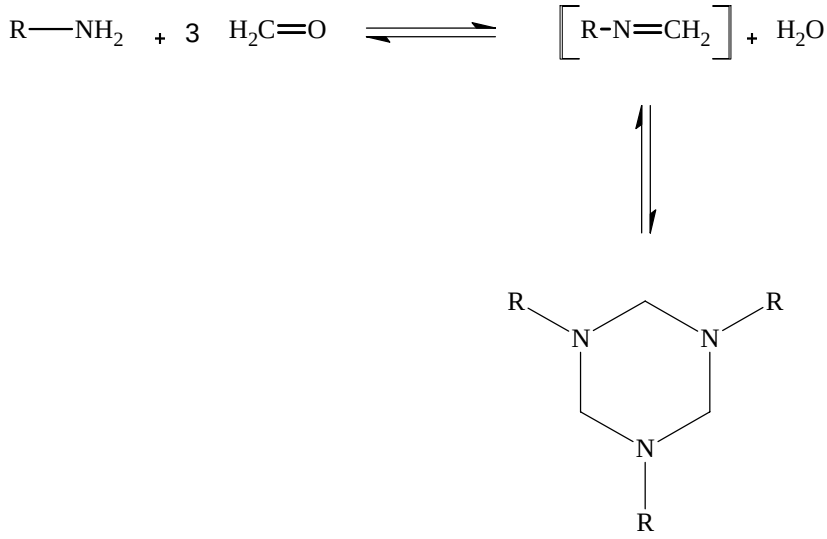
Figure 2.1 Protonation state of H_2S in aqueous solution.

In addition to its acidic properties, H_2S can also act as a nucleophile, due to the lone pairs on sulfur, and HS^- is an excellent nucleophile. It is 8 times more reactive than OH^-, 180 times more reactive than NH_3, and 125 000 times more reactive than H_2O in reaction with methyl bromide.[4]

2.2 1,3,5-Triazinanes

2.2.1 Preparation

The condensation reaction between an alkylamine and formaldehyde yields an aliphatic imine.[5] The imine is unstable and immediately cyclizes to yield the wanted 1,3,5-triazinane. The general reaction is shown in Scheme 2.2.



Scheme 2.2 Preparation of 1,3,5-triazinanes.

This condensation reaction is a common preparation method for these types of triazinanes. The structure of the side chains is determined by the structure of the primary amine used.

2.2.2 Chemical Properties

Triazinanes are cyclic amines and possess basic properties. The pK_a values of the corresponding ammonium compounds of tertiary cyclic amines are in normally in the range of 10-11.[4]

The ring carbons of the triazinane is electrophilic due to the electron withdrawing properties of the nitrogen atoms. Protonation of the nitrogen atom will enhance the electrophilic properties of the ring carbons, making the triazinane more reactive towards nucleophilic attack by H_2S and other nucleophiles.

2.2.3 Spectroscopic Data

^{1}H NMR and ^{13}C NMR data for triazinane **1** have been previously reported.[6] Triazinane **1** with numbered atoms is shown in Figure 2.2. The NMR data are given in Tables 2.2 (^{1}H NMR) and 2.3 (^{13}C NMR).

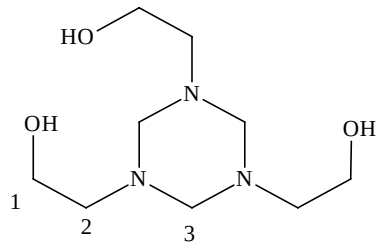


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Figure 2.2 Triazinane 1 with numbered positions.

Table 2.2 Literature ^{1}H NMR data for 1 (D_2O, rt).[6]

Chemical shift (ppm)	Multiplicity	Coupling constant *J* (Hz)	Integral	Assignment
2.69	t	5.7-5.8	0.9	H-2
3.50	s (br.)	-	0.7	H-3
3.70	t	5.7-5.8	1.0	H-1

Table 2.3 Literature ^{13}C NMR data for 1 (D_2O, rt).[6]

Chemical shift (ppm)	Assignment
54	C-2
59	C-1
74	C-3

Triazinanes are heterocyclic compounds with six ring atoms. The most stable conformation for these molecules is the chair conformation. The ring system contains two types of protons, equatorial and axial. As explained in Section 2.3.1, these two types of protons will give one singlet above the coalescence temperature (T_c), whereas they will give two doublets below T_c. The ^{1}H NMR data in Table 2.2 indicate that T_c of **1** is close to room temperature, as the two types of protons give only one signal, but it is broad and is not yet a sharp line.

In the referred work, **1** was analysed by ^{1}H NMR at -10 ^{o}C.[6] The low temperature ^{1}H NMR data are presented in Table 2.4.

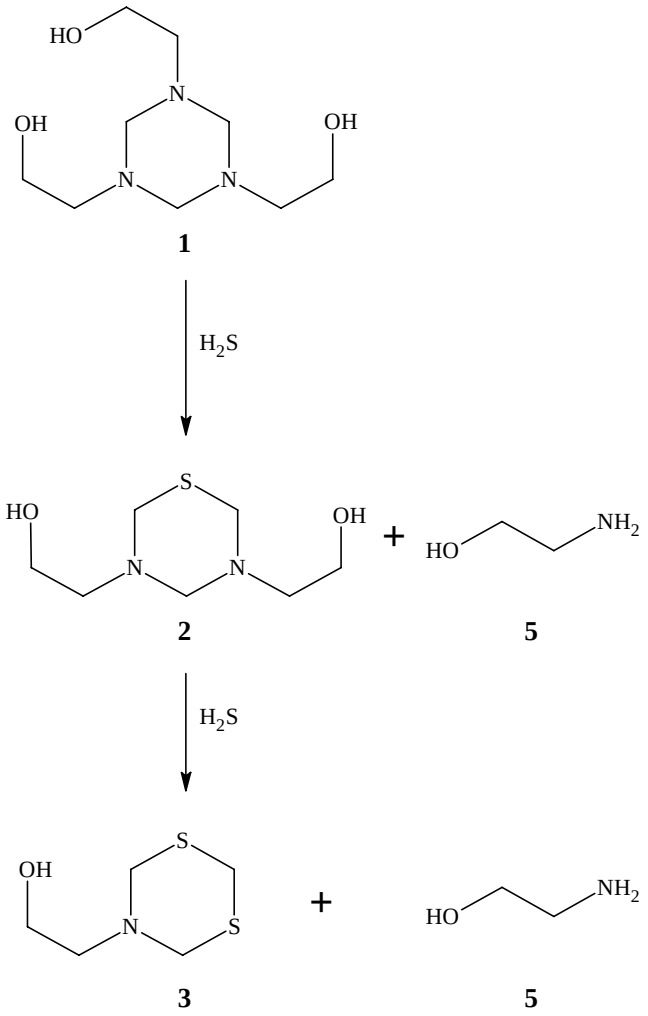
Table 2.4 ^{1}H NMR data for** 1 **(D_2O, -10 ^{o}C).[6]

Chemical shift (ppm)	Multiplicity	Coupling constant *J* (Hz)	Integral	Assignment
2.69	t	5.7-5.8	1.0	H-2
3.01	d	10.3	0.5	H-3
3.70	t	5.7-5.8	1.0	H-1
3.81	d	10.3	0.5	H-3

At -10 ^{o}C, the broad singlet found at room temperature is split into two sharp doublets. This temperature-dependent dynamic behaviour of the ^{1}H NMR signals strongly supports that **1** is a six-membered ring compound.

2.2.4 Triazinane 1 as H_2S Scavenger

Triazinane **1** is widely used as an H_2S scavenger in fields with relatively low concentrations of H_2S. It is inexpensive to use and the products of the scavenging reaction are believed to be water soluble and biodegradable.[1] Little work has been published in the area, but the main product of the reaction between **1** and H_2S is generally assumed[7,8,9] to be 5-(2-hydroxyethyl)-1,3,5-dithiazinane (**3**), presumably formed as indicated in Scheme 2.3 with the formation of 2-aminoethanol (**5**) as a by-product. Compound **5** is commonly referred to as monoethanolamine (MEA) in the natural gas industry. In this work, compound **5** will be referred to simply as ethanolamine.



Scheme 2.3 Expected formation of 3 from reaction between 1 and H_2S.

No experiments or structure determinations supporting the formation of 3,5-bis(2-hydroxyethyl)-1,3,5-thiadiazinane (**2**) are presented in the literature. However, the formation of 5-(2-hydroxyethyl)-1,3,5-dithiazinane (**3**) from 2-aminoethanol (**5**), formaldehyde and H_2S have been reported.[10] According to the same reference, **3** is used as a bactericide for suppressing the growth of sulfate-reducing bacteria, especially in well waters in the petroleum industry.

Two methods for regeneration of the triazinane after reaction with H_2S have been reported. The first used a catalyst and O_2 to regenerate **1** from dithiazinane **3**, as illustrated in the flow sheet below.[7]

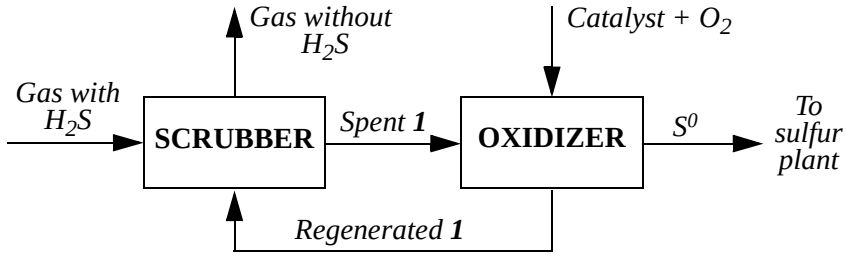
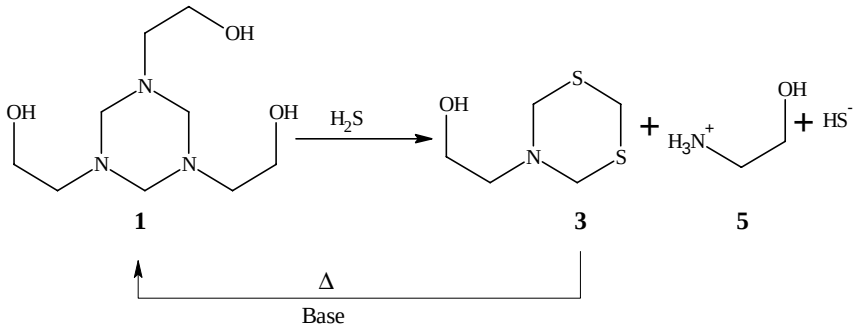


Figure 2.3 Flow sheet for regeneration of 1 in H_2S scavenging.

The second method applied very basic conditions to regenerate **1** from the products of the H_2S scavenging. The reaction is illustrated in Scheme 2.4.[8]



Scheme 2.4 Regeneration of 1 from 3 under basic conditions.

The reaction between **1** and H_2S yielded the dithiazinane **3** and ethanolamine (**5**). Addition of a base (e.g. NaOH) to the reaction mixture and heating to moderate temperatures (typically 70 °C) regenerated **1** from its products. The sulfur atoms in the ring were replaced by the nitrogen atom of **5**, and triazinane **1** is regenerated. The cycle was repeated up to ten times.

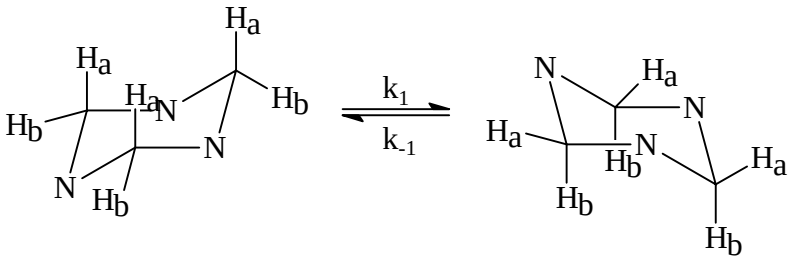
2.3 NMR Spectroscopy

2.3.1 Dynamic NMR Spectroscopy

The term dynamic NMR spectroscopy (DNMR) is used when nuclei (e.g. protons) can change back and forth between positions with different shielding

values. These protons will be chemically and magnetically non-equivalent and can be distinguished in ^{1}H NMR spectroscopy at the right conditions.[12]

For saturated 6-membered rings, the chair conformation is the most stable. These molecules have two different kinds of protons: axial and equatorial. These two positions have different shielding values, making the two kinds of protons magnetically non-equivalent and distinguishable in ^{1}H NMR spectroscopy. However, ring-flip of the molecule causes the protons to exchange between axial and equatorial position, see Scheme 2.5. The rate constants k_1 and k_{-1} in the scheme increase with temperature.



Scheme 2.5 Ring-flip of a triazinane in chair conformation. The substituents on nitrogen have been omitted for clarity.

At low temperatures in ^{1}H NMR, the two types of protons appear as two separate signals in the spectrum because the ring-flip is slow. When k_1 and k_{-1} increase with temperature, the two signals approach each other, and at a certain temperature the two signals are no longer separated. This temperature is called the coalescence temperature, and above this temperature the ring-flip is so rapid that the protons are indistinguishable by ^{1}H NMR.

2.3.2 NOE Spectroscopy

When a particular signal frequency in NMR spectroscopy is irradiated, the signal will become less intensive in the spectrum. A saturation of the signal implies that the signal disappears completely. This technique can be used to suppress unwanted signals in ^{1}H NMR, but it can also be used to achieve structural information about molecules that would be unachievable by simpler NMR methods. More specifically, irradiation of a particular signal in ^{1}H NMR spectroscopy may cause a change in signal intensity for other protons close in

space (less than 3 Å)[12] to the orignial protons, due to an effect referred to as the Nuclear Overhauser Effect (NOE).

In ^{1}H NMR spectroscopy, the NOE effect can give valuable structural information because an observable change in intensity of one signal as a consequence of the irradiation of another signal shows that these protons are close to each other. Experimentally, this is done by first recording a ^{1}H NMR spectrum without irradiation. When the desired signal is irradiated, magnetization is transferred between the irradiated nucleus and nuclei that are close to the irradiated nucleus in space. After a delay, a new spectrum is recorded. The two spectra are subtracted from each other, yielding a spectrum in which only changes in signal intensity are visible. The irradiated signal will appear as a strong negative signal, whereas any proton close in space to the original one may give a small positive or negative signal in the subtraction spectrum. NOE is usually reported as a percent change in signal intensity. The observed NOE may accidentally be zero, even though two protons are close to each other in space. However, an observable change in intensity of a signal due to the irradiation of another signal in the ^{1}H NMR spectrum strongly indicates that these two protons are close to each other in space.

- Part I -

Qualitative Investigations of the Reaction between Triazinane 1 and H_2S

The reaction between **1** and H_2S was expected to be dominated by two competing reactions:

1) Hydrolysis of **1**

2) Nucleophilic attack of HS^- on the electrophilic ring carbons in **1**

Both reactions were assumed to need activation of the triazinane ring and to take place only below a certain pH (the pK_a of **1**). With the fulfilment of this requirement, both reactions were expected to take place, but at different reaction rates. The products of the faster reaction would dominate the reaction mixture. However, since only the second reaction involved reaction with (and removal of) H_2S, the scavenging process would be most efficient at pHs where the nucleophilic attack was favoured over the hydrolysis.

Therefore, it was desirable to examine the two reactions and determine which one will dominate, given a set of reaction conditions - the most important parameter being pH.

But first, attention had to be given to the qualitative prospects of the reactions. The identification of the products of the two reactions was necessary in order to achieve a better understanding of the scavenging process. The products of the hydrolysis might still be able to react with H_2S, and hence the hydrolysis might not reduce the efficiency of **1** as much as anticipated. Also, one or more of the reaction products might be toxic and should be treated accordingly.

The easiest way to examine the questions raised above was to investigate the two reactions separately. The hydrolysis reaction was examined using water solutions of triazinane **1** alone, and the reaction initiated by the nucleophilic attack was examined by reacting **1** with Na_2S or NaHS. The replacement of H_2S with Na_2S or NaHS made it possible to run the reaction at a high pH where the hydrolysis was slow enough to be neglected. It also made it easier to control the reaction stoichiometrics and the amounts of products formed.

Finally, replacing gaseous H_2S with the sodium salts gave a safer working environment in the laboratory.

The hydrolysis of **1** will be discussed in Chapter 3 and its reaction with Na_2S and NaHS in Chapters 4 and 5.

3 The Hydrolysis of Triazinane 1

The efficiency of **1** as an H_2S scavenger is reduced by hydrolysis of the compound at moderate to low pH. It was necessary to investigate this reaction in detail to determine the impact of this process on the overall H_2S removal. Studies on the rate of hydrolysis of **1** were initiated by Dr. Jaroslav Riha in 1998. In this chapter, the structure of the hydrolysis products and the rate of hydrolysis have been investigated by NMR spectroscopy. All experimental details concerning the hydrolysis of **1** are given in Section 9.3. Spectroscopic data of pure compounds are presented in Appendix A.

3.1 The Structures of the Products

3.1.1 Results and Discussion

Compound **1** was synthesized as described in Section 9.2. An aqueous solution of **1** was acidified to pH 1.5 in order to hydrolyse the compound completely. The ^{1}H NMR spectrum of the resulting mixture is shown in Figure 3.1.

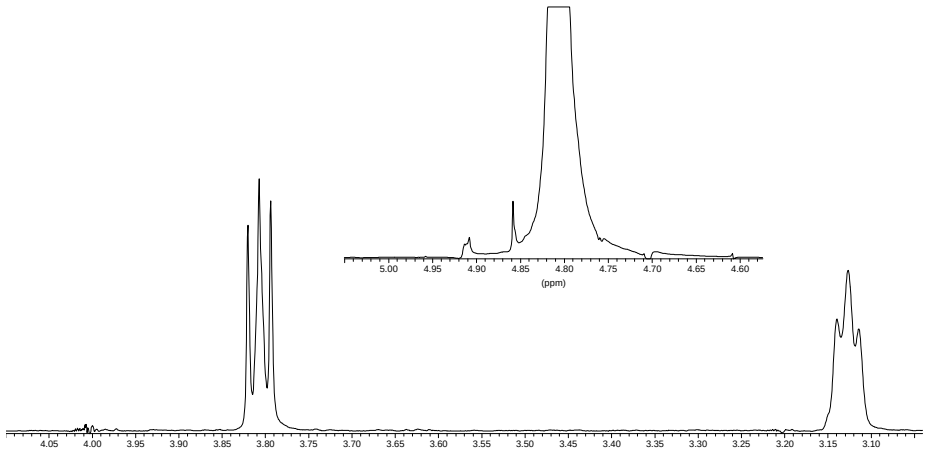


Figure 3.1 ^{1}H NMR of hydrolysed 1 (400 MHz, D_2O).

The two triplets at δ 3.13 and 3.81 ppm indicate that the main hydrolysis product consists of two neighbouring methylene groups in which the protons are coupled to each other. A ^{1}H NMR analysis of ethanolamine (**5**) alone in D_2O showed two triplets at δ 2.73 and 3.61 ppm. A large decrease in pH was expected to significantly increase these shift values because of the protonation of the ethanolamine nitrogen. Therefore, a ^{1}H NMR spectrum of ethanolamine (**5**) at pH 1.5 was recorded. The ^{1}H NMR analysis showed two triplets at δ 3.13

and 3.81 ppm. This indicated that one of the main products of the hydrolysis was indeed ethanolamine (**5**).

Formaldehyde in aqueous solution is present in its hydrated form, $CH_2(OH)_2$, and has a ^1H NMR shift value of δ 4.83 ppm in D_2O, but the large water signal interferes with the formaldehyde singlet. At low concentrations the singlet cannot be observed at all. In Figure 3.1, a small signal is observed within the water signal. The presence of this signal might indicate that hydrated formaldehyde was present in the solution, but such a conclusion could not be made without further evidence. In ^{13}C NMR there is no water signal interfering with other signals, and the hydrated formaldehyde can be detected properly. Formaline alone in D_2O gave a signal at δ 84.6 ppm in ^{13}C NMR. The hydrolysed **1** was analysed by ^{13}C NMR spectroscopy. The spectrum showed three signals at δ 44.2, 60.6 and 84.7 ppm. The first signal is assigned to the H_2N-$\underline{C}H_2$-group of **5**. The second signal arises from the -$\underline{C}H_2$-OH carbon of **5**. The third signal is assigned to the $\underline{C}H_2(OH)_2$ carbon of hydrated formaldehyde.

By these NMR experiments it is concluded that the products of the hydrolysis of **1** are ethanolamine (**5**) and hydrated formaldehyde.

3.2 The Rate of Hydrolysis

3.2.1 Kinetic Equations

The hydrolysis of a 1,3,5-triazinane (T) is assumed to have the following rate expression:

$$-\frac{d[T]}{dt} = k_1[T] + k_2[T][H^+] \tag{3-1}$$

For reactions run at constant pH, $[H^+]$ is constant, and Equation 3-1 is simplified to

$$-\frac{d[T]}{dt} = k_{obs}[T] \tag{3-2}$$

with

$$k_{obs} = k_1 + k_2[H^+] \tag{3-3}$$

Solving the differential Equation 3-2 yields the following expression:

$$-\ln[T] = k_{obs}t + C \tag{3-4}$$

The initial conditions are set to [T] = $[T]_0$ when the time t = 0, and Equation 3-4 is rearranged to

$$\ln\frac{[T]_0}{[T]} = k_{obs}t \tag{3-5}$$

Hence, for any first order reaction, a plot of ln([T]/$[T]_0$) against time will give a straight line with a slope equal to k_{obs} if Equation 3-2 applies.

According to Equation 3-3, a plot of k_{obs} versus $[H^+]$ for several different pHs will give a straight line from which k_1 and k_2 can be calculated.

The half-life of the triazinane, $t_{½}$, is a very useful property that can be calculated from k_{obs} by introducing the limiting condition [T] = 0.5$[T]_0$ when t = $t_{½}$ into Equation 3-5, which rearranges to Equation 3-6:

$$t_{1/2} = \frac{\ln 2}{k_{obs}} = \frac{\ln 2}{k_1 + k_2[H^+]} \tag{3-6}$$

3.2.2 Results and Discussion

The concentration of **1** was determined with various time intervals using an internal standard (IS) in ^{1}H NMR. Two temperatures were used, 22 °C and 60 °C. At 22 °C, the experiment was performed in the NMR tube, and NMR spectra were recorded with fixed intervals. The NMR experiments at 60 °C, in which samples were taken from a solution of **1** and quenched before the NMR analysis, were performed by Dr. Jaroslav Riha. The concentrations of triazinane **1** and the buffers used were the same in all the experiments. For each temperature, several different pH values were used, ranging from 10.9 to 8.0. In each experiment, [T] was determined by comparing the integral of a triazi-

nane signal with the integral of the IS signal. In accordance with Equation 3-5, $\ln([T]_0/[T])$ was plotted against time. An example is shown in Figure 3.2.

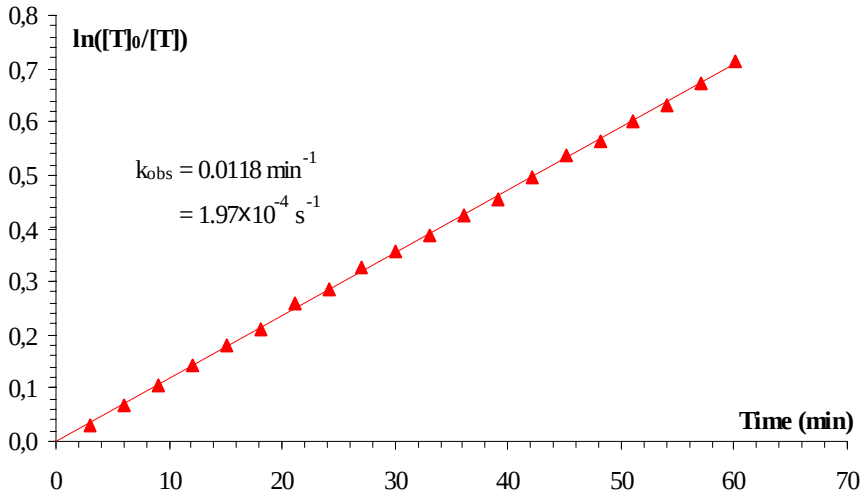


Figure 3.2 Plot of $\ln([T]_0/[T])$ against time for the hydrolysis of** 1 **at pH 10.0 and 22 °C.

From linear regression of the data at 22 °C, a very good linearity was found, showing not only that the accuracy of the measurements was very good, but also that Equation 3-2 is valid and the pH is constant. By the method used at 60 °C, fewer points were recorded, and the linearity was not as good. Moreover, the measurements at 60 °C were only successful at two pH levels, as the hydrolysis was too fast at lower pHs to be determined by the method applied at this temperature.

For both temperatures, k_{obs} was determined by linear regression of the data points in each experiment. By plotting k_{obs} against $[H^+]$ for the three pH levels at 22 °C as shown in Figure 3.3, another straight line was obtained in accordance with Equation 3-3. The rate constants k_1 and k_2 were determined from linear regression of these data points. At 60 °C, k_1 and k_2 were determined by applying Equation 3-3 to both pH values.

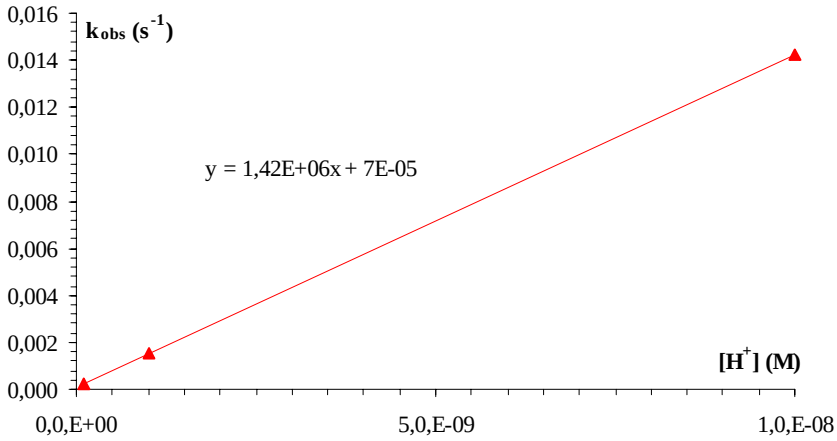


Figure 3.3 Plot of k_{obs} versus $[H^+]$ for the hydrolysis of** 1 **at 22 °C.

Half-lives of **1** were calculated from Equation 3-6. The results are given in Tables 3.1 and 3.2.

Table 3.1 Rate constants and $t_{½}$ for the hydrolysis of** 1 **at 22 °C.

pH	$[H^+]$ (M)	k_{obs} (10^{-3} s^{-1})	$t_{½}$ (10^{2} s)	k_1 (10^{-5} s^{-1})	k_2 (10^{6} $M^{-1}s^{-1}$)
10.0	1.0×10^{-10}	0.197 ± 0.001	35.2 ± 0.2		
9.0	1.0×10^{-9}	1.51 ± 0.02	4.59 ± 0.05	7 ± 2	1.42 ± 0.01
8.0	1.0×10^{-8}	14.3 ± 0.4	0.49 ± 0.1		

Table 3.2 Rate constants and $t_{½}$ for the hydrolysis of** 1 **at 60 °C.

pH	$[H^+]$ (10^{-10} M)	k_{obs} (10^{-2} s^{-1})	$t_{½}$ (s)	k_1 (10^{-4} s^{-1})	k_2 (10^{8} $M^{-1}s^{-1}$)
10.9	0.13 ± 0.01	0.37 ± 0.01	187 ± 4	-8 ± 8	3.4 ± 0.6
9.5	3.2 ± 0.2	1.1 ± 0.1	6.3 ± 0.6		

In both cases the value for k_2 is several magnitudes larger than the value for k_1. At 60 °C, k_1 could not be accurately determined from Equation 3-3, but neglecting the k_1 term in Equation 3-1 will give very small errors under normal conditions (pH<10). At 22 °C, k_1 only became significant when pH was very high (close to 10 or higher), but at this temperature the determination of k_1 was more accurate.

Standard deviations in the regressions that gave k_{obs}, k_1 and k_2 were obtained from the regression tool in Microsoft Excel 1997, except for the calculation of k_1 and k_2 at 60°C, for which Equation B-6 in Appendix B was used to determine the uncertainty. It was assumed that possible errors in the measured volumes, errors in the NMR integrals and errors in pH recordings were all random errors that would be reflected in the regression standard deviation. The uncertainties in the observed rate constants were found to be up to 10 % for the experiments at 60 °C, and up to 4 % for the experiments at 22 °C. At 60 °C, the uncertainties in k_1 and k_2 were found to be 100 % and 18 %, respectively. At 22 °C, the uncertainties were 29 % for k_1 and less than 1 % for k_2. The very large margin of error in k_1 is explained by the fact that k_1 is found from the intersection between the graph in Figure 3.3 and the y-axis. This value is very close to zero, and small changes in the data from which the graph is made will have a much larger impact on the point of intersection than on the slope of the line, which determines k_2. The uncertainties in the calculated half-lives were determined from Equation B-6 in Appendix B and were found to be up to 10 % for the experiments at 60 °C, and up to 4 % for the experiments at 22 °C.

The results in Tables 3.1 and 3.2 can be used to give reliable predictions of the rate of hydrolysis of **1** at other reaction conditions, as long as the pH is kept at a level where k_1 is negligible. At both temperatures, the pH should be below 10 for the accuracy of the predictions to be acceptable.

The calculated half-lives of **1** are represented graphically in Figure 3.4. The plot is simple and gives useful information about the stability of triazinane **1** when optimal reaction conditions for the H_2S scavenging are to be found.

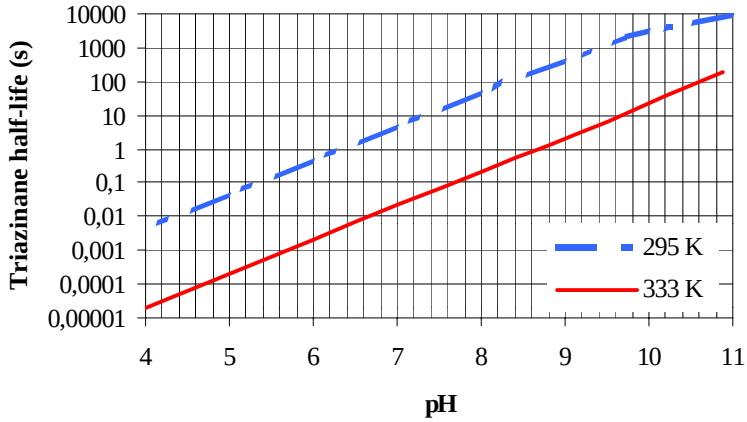


Figure 3.4 Half-life of 1 as a function of pH at two different temperatures.

3.3 Conclusion

When **1** was hydrolysed in aqueous solution, NMR spectroscopy showed that ethanolamine (**5**) and formaldehyde dihydrate were formed.

Using an internal standard in ^{1}H NMR spectroscopy, the rate of hydrolysis at two different temperatures was determined.

The final rate expressions for the hydrolysis of **1** are:

At 22 °C: $$-\frac{d[T]}{dt} = 1.42\times10^{6}[T]\ [H^{+}] \qquad \text{pH} < 10 \qquad (3\text{-}7)$$

At 60 °C: $$-\frac{d[T]}{dt} = 3.4\times10^{8}[T]\ [H^{+}] \qquad \text{pH} < 10 \qquad (3\text{-}8)$$

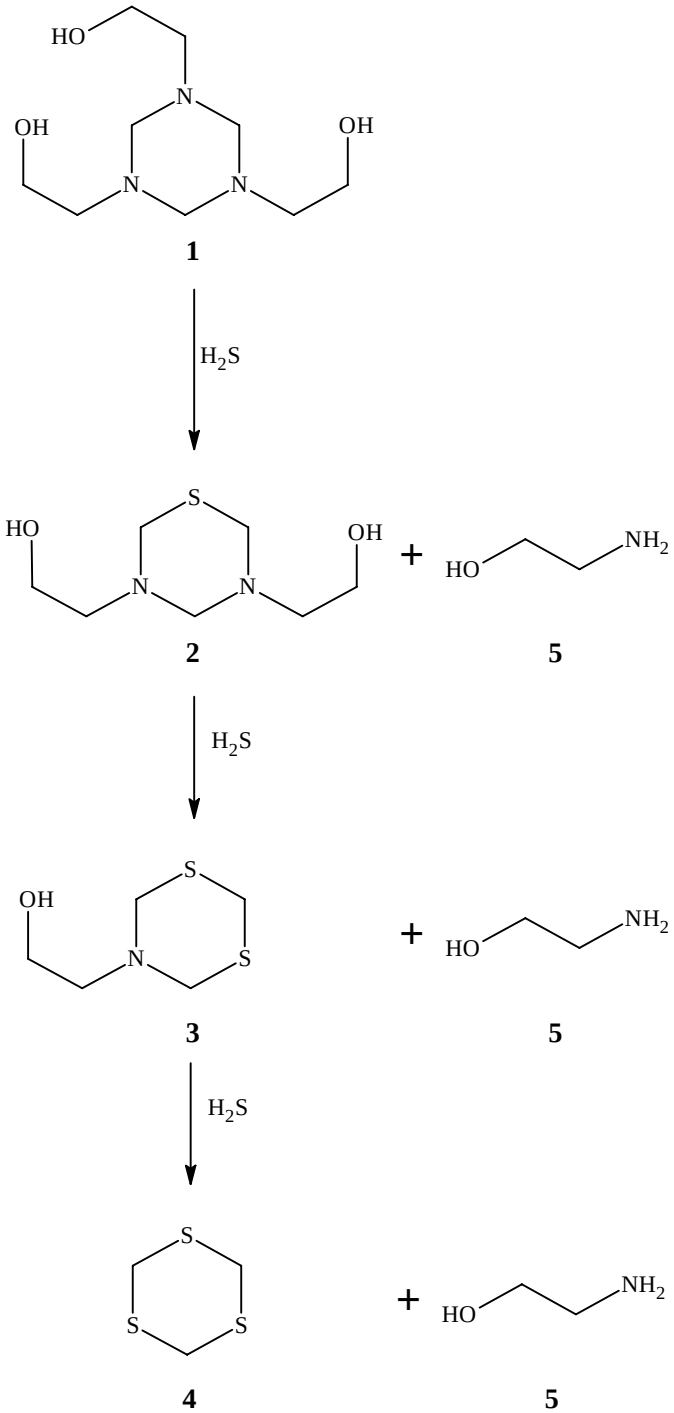
4 The Equimolar Reaction between Triazinane 1 and HS^-

When the nature of the hydrolysis of triazinane **1** had been established in terms of both rate and products of hydrolysis (see Chapter 3), the reaction between **1** and H_2S could be examined. The goal of this chapter was to identify the reaction products of the H_2S scavenging reaction. Hence, the experiments were performed at a high pH in order to avoid the hydrolysis. According to Figure 3.4, **1** has a half-life of about 1 hour at pH 10. At this pH, the reaction between **1** and HS^- is fast enough for the hydrolysis of **1** to have an insignificant impact on the experiments. Therefore, the identification of the reaction products in the reaction was done at pH 10, using Na_2S or NaHS instead of H_2S. When the reaction products had been identified, **1** was reacted with gaseous H_2S, and the results were compared with the results of the reaction with Na_2S (see Chapter 5).

According to the literature, dithiazinane **3** and ethanolamine (**5**) are the products of the reaction between **1** and H_2S.[7,8,9] Thiadiazinane **2** and trithiane **4** may also be found in the reaction mixture if **3** is formed as indicated in Scheme 4.1.

Initially, triazinane **1** was reacted with only one equivalent of Na_2S to reduce the number of products. The analyses done on the reaction products are presented in Sections 4.1 to 4.4. The reactions between **1** and more than one equivalent of Na_2S or pure H_2S are discussed in Chapter 5.

All experimental details are given in Section 9.4.



Scheme 4.1 Expected course of reaction between 1 and H_2S.

4.1 NMR Analyses

Na_2S (1 equivalent) was added to a buffered, aqueous solution of **1** (1 equivalent) at pH 10 and room temperature. The reaction was monitored by ^1H NMR spectroscopy. Most of **1** had reacted after 45 minutes when the first spectrum was recorded. The pH of the solution increased slightly as the reaction proceeded. This indicated that protons were consumed during the reaction.

4.1.1 ^1H NMR and ^1H,^1H COSY Spectra

A ^1H NMR spectrum of the reaction mixture is shown in Figure 4.1.

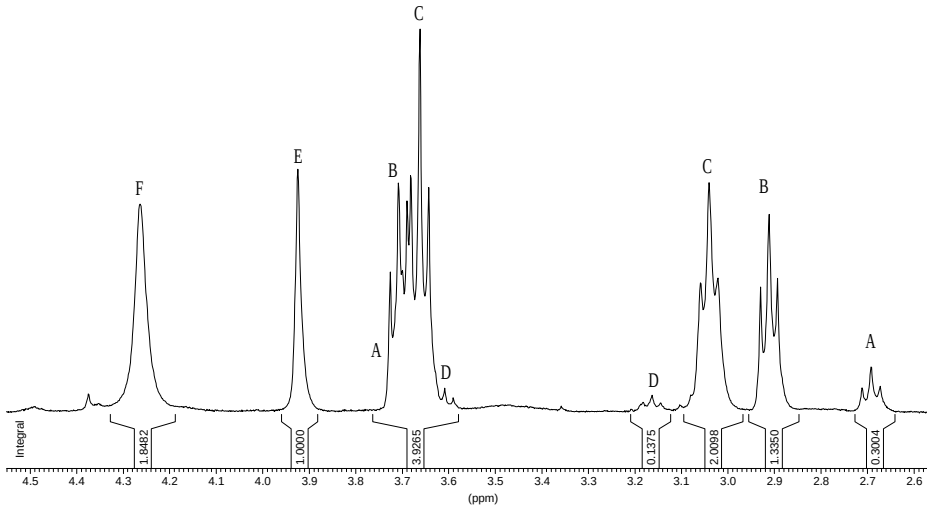


Figure 4.1 ^1H NMR spectrum of reaction mixture (300 MHz, D_2O, pH 10).

A ^1H,^1H COSY spectrum was recorded in order to establish which signals were coupled to each other. The results are presented in Table 4.1.

Table 4.1 ^1H NMR data for the reaction mixture (300 MHz, D_2O, pH 10).

δ (ppm)	Multiplicity	Coupling constant *J* (Hz)	Integral	Coupled to signal at δ (ppm)	Spin system
2.69	t	5.7-6.0	0.30	3.70	A
2.91	t	5.3-5.7	1.33	3.71	B
3.04	t	5.7	2.01	3.66	C
3.16	t	5.7	0.14	3.61	D
3.61	t	5.7	3.93	3.16	D
3.66	t	5.7-6.0		3.04	C
3.70	t	-		2.69	A
3.71	t	5.3-5.7		2.91	B
3.92	s	-	1.00	-	E
4.26	s	-	1.85	-	F

4.1.2 1D NOE spectra

Some of the spin systems A-F in Table 4.1 might be parts of the same compound although $^1H,^1H$ COSY did not indicate a coupling. In NOE spectroscopy (see Section 2.3.2), protons that are close to each other in space can be correlated. In the case of triazinane **1** and the products from its reaction with Na_2S, NOE might be observed between protons bonded to carbon atoms that are separated by a heteroatom.

The signals at δ 4.26 (spin system F in Table 4.1), 3.92 (spin system E), 3.66 (spin system C) and 3.04 ppm (spin system C) were irradiated in a 1D NOE experiment. The results are given in Table 4.2 as percent increase in signal intensity.

Table 4.2 NOE effect for selected signals (400 MHz, D_2O, pH 10).

Signal irradiated (ppm)	% increase of signal			
	3.04 ppm	**3.66 ppm**	**3.92 ppm**	**4.26 ppm**
3.04	-	6.3	5.8	1.6
3.92	3.2	-	-	-
4.26	1.5	2.8	2.0	-

Irradiation of the signal at 3.66 ppm also gave irradiation of the other signals in the multiplet, and the 1D NOE experiment was inconclusive for this signal.

The results show that spin systems C, E and F, and accordingly the four signals at δ 3.04, 3.66, 3.92, and 4.26 ppm, can all be assigned to the same compound, compound C. Spin systems A, B and D are the only spin systems in their respective compounds, henceforth referred to as compounds A, B and D.

4.1.3 ^{13}C NMR and HETCOR Spectra

Some of the shifts in the ^{1}H NMR spectrum are highly dependent on the pH of the solution. Therefore, identifying the compounds simply by comparing the ^{1}H NMR data with that of the pure compounds is an unreliable method. A better way to identify the components of the reaction mixture is to compare ^{13}C NMR shifts because they are less dependent the pH of the solution. Hence, a ^{13}C NMR spectrum of the reaction mixture was recorded. The spectrum is shown in Figure 4.2.

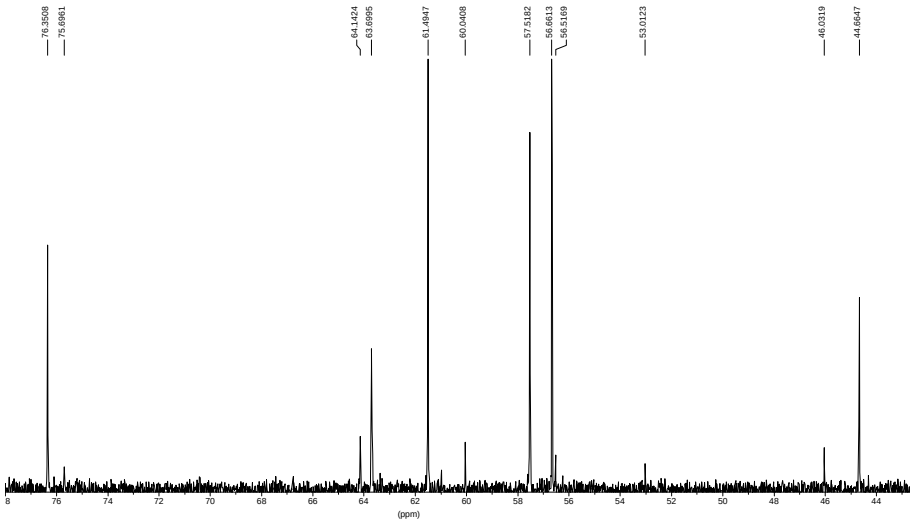


Figure 4.2 ^{13}C NMR spectrum of the reaction mixture (75 MHz, D_2O, pH 10).

A HETCOR spectrum was recorded in order to correlate the different protons in the ^{1}H NMR spectrum with their respective carbon atoms. The results are given in Table 4.3.

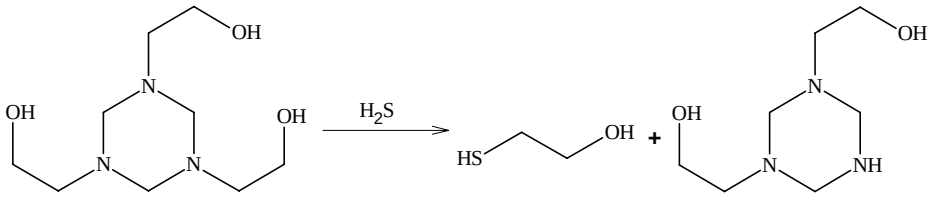
Table 4.3 ^{13}C NMR data for the reaction mixture (75 MHz, D_2O, pH 10).

δ (ppm)	Couples to ^1H NMR signal at δ (ppm)	Compound assignment
44.7	2.91	B
46.0	-	(D)
56.5	2.69	A
56.7	3.04	C
57.5	4.26	C
60.0	-	(A)
61.5	3.66	C
63.7	3.71	B
64.1	3.61	D
75.7	-	(A)
76.4	3.92	C

Some of the ^{13}C signals were too weak to show $^1H,^{13}C$ coupling, but by comparison with ^{13}C and ^1H NMR spectra of the pure compounds (see Appendix B) and the method of elimination, they were given the compound assignments in parentheses.

4.1.4 Investigation of Possible Products

Other products than compounds **1** to **5** from Scheme 4.1 were considered as possible components of the reaction mixture. A nucleophilic attack on the 1-carbon of the hydroxyethyl side-chain would result in the formation of 2-mercaptoethanol (**6**) as shown in Scheme 4.2.



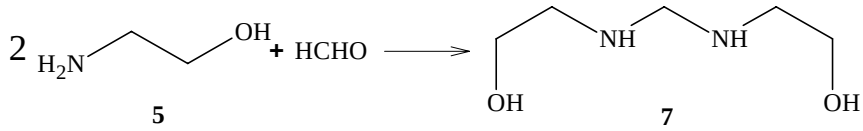
1 **6**

Scheme 4.2 Possible formation of 2-mercaptoethanol (6) from 1 and H_2S.

A ^1H NMR analysis of **6** at pH 10 showed two triplets at δ 2.66 and 3.65 ppm with a coupling constant J = 6.1-6.3 Hz. In ^{13}C NMR, two signals were found at δ 28.8 and 66.4 ppm. The chemical shifts and coupling constant of this com-

pound did not match the experimental NMR data of Tables 4.1 and 4.3. It was concluded that 2-mercaptoethanol was not found in the reaction mixture, and that nucleophilic attack on the hydroxyethyl side-chain of triazinane **1** did not take place. This result was not surprising, as the ring carbons are clearly more electrophilic than the carbons of the side-chain.

Before the NOE experiment was performed, calculations[11] of ^{13}C NMR shifts indicated that 2,2'-[methylenebis(imino)]diethanol (**7**) was a possible product that matched the experimental NMR data of spin systems C and E (Table 4.1). It may be formed from two equivalents of ethanolamine (**5**) and one equivalent of formaldehyde (present to some extent in the triazinane reagent).



5 **7**

Scheme 4.3 Possible formation of 2,2'-[methylenebis(imino)]diethanol (7) from 5 and formaldehyde.

An attempt to synthesize compound **7** from one equivalent of formaldehyde and two equivalents of ethanolamine (**5**) was unsuccessful. ^1H NMR spectra of the reaction mixture showed that half of the ethanolamine (**5**) had reacted with formaldehyde to form triazinane **1**, and the rest was unreacted. Increasing the amount of ethanolamine (**5**) to four equivalents only increased the amount of unreacted **5**. An important notice with respect to the assignment of compound D in the next section is that traces of the compound was found in these NMR spectra. This experiment shows not only that **1** is extremely easily formed whenever formaldehyde and ethanolamine (**5**) is jointly present, it also excludes compound **7** from being a product of the reaction between triazinane **1** and HS^-.

4.1.5 Assignment of NMR Data

The NMR experiments resulted in ^1H and ^{13}C NMR data for the four different components of the reaction mixture, compounds A-D. The ^1H NMR spectrum with compound assignments are given in Figure 4.3.

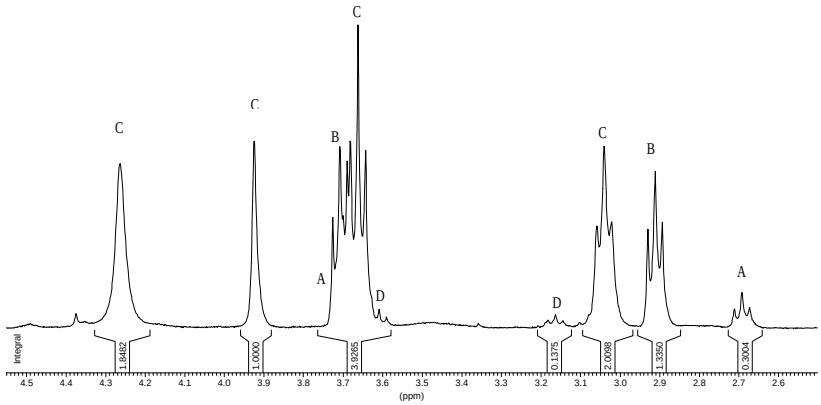


Figure 4.3 ^1H NMR spectrum of reaction mixture with compound assignments (300 MHz, D_2O, pH 10).

Compound A

The weak ^{13}C NMR signals at δ 56.5, 60.0 and 75.7 ppm are recognized as unreacted **1** by comparison with a ^{13}C NMR spectrum of **1** alone (see Section 9.2 or Appendix A). Unreacted **1** is seen in the ^1H NMR spectrum in Figure 4.3 as the small triplet at δ 2.69 ppm. The other triplet that belongs to **1** is normally located at 3.70 ppm, and in this spectrum it is located inside the multiplet at 3.64-3.72 ppm. The broad singlet at 3.49 ppm is barely visible in this spectrum. Hence, compound A is identified from unreacted **1**. According to the integrals in Figure 4.3, 4 % of the reaction mixture after 45 minutes is unreacted **1**.

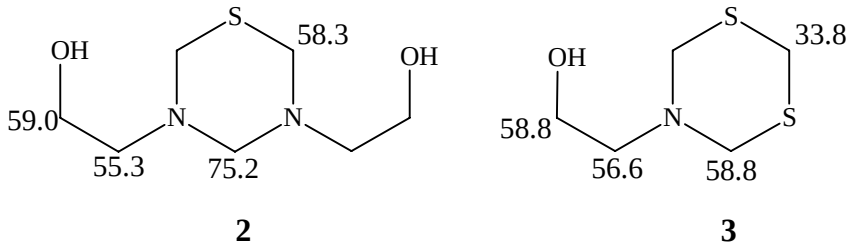
Compound B

Ethanolamine (**5**) is likely to be formed when **1** reacts with a nucleophile. Compound B is found in the ^{13}C NMR spectrum at δ 44.7 and 63.7 ppm (see Appendix A) and is identified as monoethanolamine (**5**). This compound constitutes 52 % of the reaction mixture after 45 minutes, some of which was already present in the synthesized triazinane **1**.

Compound C

According to Scheme 2.3 thiadiazinane **2** and/or dithiazinane **3** are likely to be formed in the reaction between **1** and H_2S. The hydroxyethyl chain of both compounds will give two triplets of equal integrals in the ^1H NMR spectrum. Both compounds will additionally give two singlets from the ring protons, one twice as large as the other. In the case of the thiadiazinane **2**, the relative integrals of the four signals will be 2:2:2:1. For dithiazinane **3**, the relative integrals will be 1:1:1:2. In Table 4.1, the integrals of compound C are roughly 2:2:1:(unknown). This indicates that compound C might be thiadiazinane **2**. This corresponds well with the assumption that the equimolar stoichiometry of the reaction favours the formation of **2** over the formation of **3**. Another feature that is worth noting is that the two ^1H NMR signals from the ring carbons in **2** appear as very sharp signals compared to the signal from the triazinane **1** ring carbons, which is very broad and barely visible in the spectrum. This indicates that **2** has a faster ring-flip at room temperature, which may be explained by the reduced steric hindrance for the ring-flip in **2** compared to **1**, which has one more hydroxyethyl substituent.

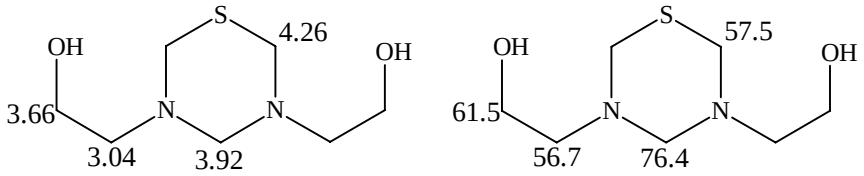
The ^{13}C NMR shift values for thiadiazinane **2** and dithiazinane **3** were calculated, and the results are presented in Figure 4.4.[11]



2 **3**

Figure 4.4 Calculated ^{13}C NMR shifts (ppm) for compounds 2 and 3.

By comparison with the results presented in Table 4.3, it is clear that structure **2** corresponds best with experimental ^{13}C NMR data. The ^1H and ^{13}C NMR data of structure **2** are assigned as shown in Figure 4.5.



a **b**

Figure 4.5 Experimental ^1H (a) and ^{13}C (b) NMR shifts (ppm) assigned to structure 2.

Altogether, the experimental NMR data of compound C in the reaction mixture corresponds well with expected values for thiadiazinane **2**. This compound constitutes 39 % of the reaction mixture after 45 minutes.

Compound D

The spin system D in Table 4.3 has two triplets in the ^1H NMR spectrum. The coupling constant and shift values of the two triplets indicate that compound D is a derivative of ethanolamine (**5**), probably of the form X-CH_2-CH_2-Y, where X and Y are R_2N- or RO-groups. The compound is polar (see Section 4.2.1) and does not contain sulfur, as it also appears in spectra of solutions containing triazinane **1** and ethanolamine (**5**), but no sulfide source (see section 4.1.4). It is, however, a relatively small part of the reaction mixture (5 % according to the integrals in Table 4.1), and no effort was made to determine its structure by isolating the compound from the reaction mixture.

4.2 Separation and Isolation of the Products

Even though the NMR analyses of the reaction mixture from the equimolar reaction between **1** and Na_2S correspond well with thiadiazinane **2** and ethanolamine (**5**) being the two main products, a mass analysis was desirable to confirm these findings. GC-MS would give mass spectra of each component in the mixture, but this method requires that the components can be separated by gas chromatography (GC) and that they are sufficiently stable for the molecular ion to be observed in electron impact mass spectrometry (EIMS). The results of the GC analyses of the various components in the mixture are presented in Section 4.2.2.

Other methods, e.g. elemental analysis or direct inlet EIMS, can only be applied to the pure compounds, and so it was necessary to separate and isolate

the main products. The attempts made to perform this isolation are described in Sections 4.2.1 and 4.2.3. Yet another method, short path distillation, is discussed in Section 5.3.3.

4.2.1 Liquid/Liquid Extraction

The reaction mixture from the equimolar reaction between **1** and Na_2S was an aqueous solution containing unreacted **1**, ethanolamine (**5**), compound C and traces of the unknown compound D. Compound C was the main product of the reaction, and the experimental NMR data corresponded best with the structure of thiadiazinane **2**. There was a possibility that **2** could be separated from **1** and ethanolamine by polarity, and the aqueous reaction mixture was extracted with dichloromethane. In this manner, thiadiazinane **2** and small amounts of an unknown compound later identified as dithiazinane **3** (see Section 5.4) was separated from the mixture. Compound **3** was not a part of the original mixture and had been formed during the extraction. The fractions that contained both **2** and **3** were purified by evaporating the dichloromethane, dissolving the resulting yellow oil in water and performing extractions with smaller portions of dichloromethane. The portions that contained only **2** were combined, and **2** with a purity of 90 % was obtained after evaporation of the solvent. In later experiments, **2** was isolated by continuous extraction with dichloromethane.

Triazinane **1**, ethanolamine (**5**) and compound D are more polar compounds than **2** and **3**, and mainly remained in the water phase although traces of **5** was found in the last portions. The product, **2**, was a yellow, viscous liquid, similar in appearance to triazinane **1**. The synthesis and isolation of **2** have not yet been reported in the literature.[13] Obtained purities were typically between 70 and 85 % from ^{1}H NMR spectroscopy, but by repeating the purification by extraction, purities of up to 90 % for the isolated **2** was obtained. ^{1}H NMR spectroscopy showed that dichloromethane, dithiazinane **3** and small traces of triazinane **1** were the main impurities. The final traces of dichloromethane were very difficult to evaporate off due to the high viscosity of the isolated liquid.

4.2.2 Gas Chromatography

Separation of the different components by gas chromatography would serve two causes: the opportunity to follow the reaction between **1** and Na_2S by GC in addition to NMR, and the possibility that the products can be separated and analysed by GC-MS. Both applications require that the starting materials as

well as the products can be analysed by GC. The various pure components were analysed separately to establish if GC was a suitable method for the analysis of these compounds.

Amines are known to be difficult to analyse by gas chromatography. Triazinane **1** is also a very polar compound due to its three OH-groups. Several attempts to get a solution of **1** in dichloromethane through a GC column (GC system number 1, Section 9.1.2) were unsuccessful. A column especially designed for the analysis of amines was provided, and triazinane **1** in both dichloromethane, methanol and water were attempted analysed by GC system number 2 (Section 9.1.2). Again, no peaks were found in the chromatograms.

Ethanolamine (**5**) was also analysed on both systems, and the chromatograms showed a splitted peak at about 3.6 minutes. This is a shorter retention time than expected for a such a polar compound, and the splitting of the peak was very surprising. No obvious explanation for this behaviour was found, but it was concluded that ethanolamine (**5**) could not be satisfactorily analysed by GC.

Thiadiazinane **2** was isolated as described in Section 4.2.1. The pure compound in dichloromethane was injected into GC system number 2. No peak was observed in the chromatogram. Apparently, both triazinane **1** and thiadiazinane **2** are too polar to go through the GC column.

Altogether, the attempts to analyse the reaction by GC were unsuccessful as none of the main components could be satisfactorily analysed. Moreover, it was concluded that the reaction between **1** and Na_2S could not be followed by GC. Hence, GC-MS could not be used to obtain mass spectra of the products.

The analysis of dithiazinane **3** by GC is discussed in Section 5.3.2.

4.2.3 Thin Layer and Column Chromatography

Thin layer chromatography (TLC) is the simplest of the chromatographic methods. A TLC analysis of the reaction mixture from the reaction between **1** and HS^- would be a simple way of finding out if the components in the reaction mixture can be separated based on polarity.

A reaction mixture from the equimolar reaction between **1** and Na_2S in methanol was applied to five TLC plates. Five different mobile phases were employed: methanol, methanol/ethyl acetate (1:4), ethyl acetate, acetonitrile

and hexane. Acetonitrile and ethyl acetate were selected as the best mobile phases for this separation, as one of the compounds was very well separated from the others using these mobile phases, with $\Delta R_f = 0.56$ for acetonitrile and 0.35 for ethyl acetate.

The TLC experiments indicated that at least one compound could be isolated by column chromatography. A new experiment was performed, in which the reaction mixture of the equimolar reaction between **1** and Na_2S was eluated with ethyl acetate through a silica column. The fractions containing the single spot from the TLC analyses were analysed by ^1H NMR. The spectrum showed a product that was later identified as dithiazinane **3** (see Section 5.4). This compound was not a part of the original reaction mixture but had been formed during work-up.

4.3 Analyses of Thiadiazinane 2

4.3.1 Mass Analysis

In addition to the extensive NMR analyses presented in Section 4.1, the isolation of thiadiazinane **2** obtained by water/dichloromethane extraction made it possible to achieve a mass analysis of the pure compound. However, heterocycles like **1** and **2** are assumed to be difficult to detect in EIMS, due to the many possible fragmentations of the molecules. Elemental analysis was chosen as the preferred method.

Compound **2** has the molecular formula $C_7H_{16}N_2O_2S$. The result of the combustion analysis and the calculated composition are presented in Table 4.4.[11]

Table 4.4 Elemental analysis of thiadiazinane 2.

	C (%)	**H (%)**	**N (%)**	**O (%)**	**S (%)**
Calculated	43.7	8.4	14.6	16.6	16.7
Found	42.4	8.1	14.0	-	16.6

The reason for the relatively large difference between the calculated and observed value for carbon is explained by the presence of the two main impurities, dithiazinane **3** and dichloromethane. Dithiazinane **3** contains 36.3 % carbon whereas dichloromethane contains only 14.4 % carbon. This also explains the deviations in the values for the other elements.

In conclusion, the findings from the elemental analysis supported the NMR results. Thiadiazinane **2** was identified as one of the products of the equimolar reaction between **1** and HS^-.

4.3.2 Low Temperature ^1H NMR Spectra

As described in Section 2.3.1, the ring protons of saturated six-membered rings like triazinane **1** and its derivatives can show a different splitting pattern in ^1H NMR spectroscopy when the temperature is lowered to the coalescence temperature, T_C. In fact, if singlets like the ones at δ 3.92 and 4.26 ppm in Figure 4.1 are splitted into two doublets at low temperatures, a reasonable explanation for this behaviour would be that the signals arise from axial and equatorial protons of a six-membered ring compound.

A ^1H NMR spectrum of the isolated thiadiazinane **2** was recorded at room temperature, -15 °C, -40 °C, -53 °C, -66 °C, and -79 °C. The spectra are shown in Figure 4.6.

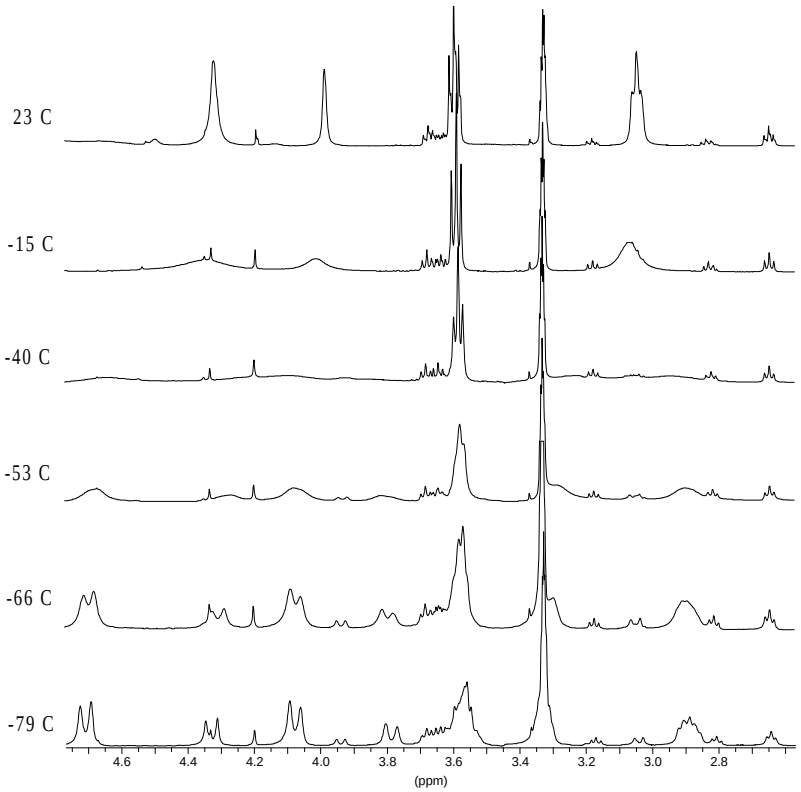


Figure 4.6 ^1H NMR spectra of thiadiazinane 2 (400 MHz, CD_3OD).

In addition to the signals from thiadiazinane **2**, a large signal from methanol at δ 3.36 ppm as well as traces of triazinane **1** and ethanolamine (**5**) were found. From the spectrum at -79 °C, it is clear that the thiadiazinane singlet located at δ 3.92 ppm at room temperature has been splitted into two distinct doublets at δ 3.79 and 4.33 ppm with a coupling constant of 13.8 Hz, indicating a geminal coupling. The same has happened to the singlet at δ 4.26 ppm, which is now found as two doublets at 4.08 and 4.71 ppm with a coupling constant of 12.8 Hz. This NMR experiment confirms that the main product of the reaction has the six-membered ring intact. Another interesting observation is that the protons of the side-chain methylene group in α-position to the nitrogen appear as two multiplets (actually two doublets split into triplets) at low temperatures. The multiplets are found at δ 2.89 and 3.33 ppm, the latter one interfering with the methanol signal. This behaviour is explained by the fact that the two protons are prochiral and magnetically non-equivalent. Both these observations are in accordance with thiadiazinane **2** being the main product.

4.3.3 IR Spectroscopy

The isolation of **2** also made it possible to achieve an IR spectrum of the pure compound. In the spectrum, both a strong O-H stretch absorption (3378 cm^{-1}) and a strong C-O stretch absorption (1048 cm^{-1}) were found, indicating that the isolated compound is an alcohol.[14] A weak C-N stretch absorption (1176 cm^{-1}) showed that the compound also contained an amine moiety.[14] Finally, a C-S stretch absorption (691 cm^{-1}) indicated the presence of a sulfur moiety.[14]

In conclusion, the results from the IR analysis supported that thiadiazinane **2** was the isolated product.

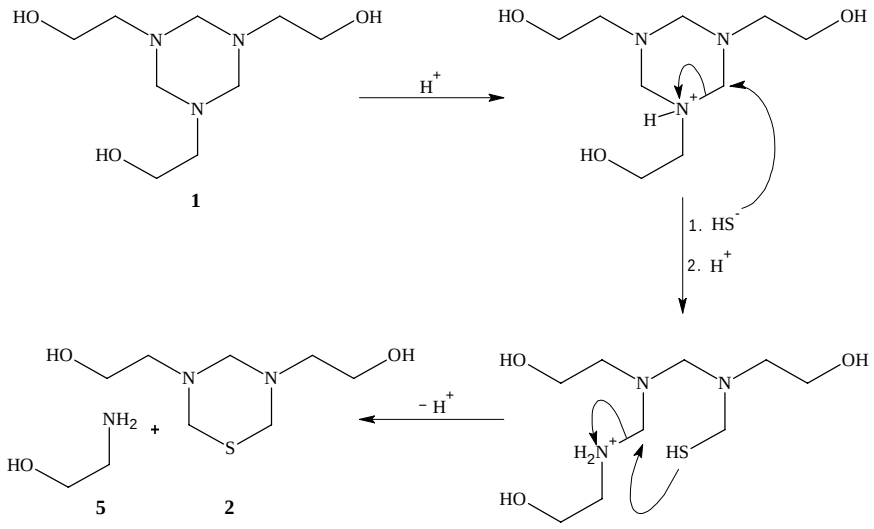
4.4 The pH-Dependence of the Reaction

Earlier work[15] has established that the reaction between **1** and Na_2S is faster at lower pH levels. In this work, the specific correlation between the reaction rate and pH is treated in Chapter 6, and it is found that a decrease in pH dramatically increases the rate of reaction. This observation indicates that protonation is a rate-determining step in the reaction mechanism. It is assumed that the reaction is initiated by the protonation of the ring nitrogen of the triazinane **1**, making the ring carbon more electrophilic and hence more reactive towards a nucleophilic attack by the sulfide nucleophile.

4.5 Conclusion

The equimolar reaction between 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane (**1**) and Na_2S in aqueous solution at pH 10 was analysed by various NMR techniques. The results indicate that a nucleophile attack on the electrophilic carbon in the triazinane ring takes place, and that ethanolamine (**5**) and 3,5-bis(2-hydroxyethyl)-1,3,5-thiadiazinane (**2**) is formed. Traces of two other products, one unknown and the other later identified as 5-(2-hydroxyethyl)-1,3,5-dithiazinane (**3**), were also found in the isolated product. Thiadiazinane **2** was isolated by liquid/liquid extraction and identified by a combination of NMR, IR and elemental analysis.

The reaction is assumed to be initiated by the protonation of the nitrogen atom, as shown in Scheme 4.4. A nucleophilic attack by the sulfide nucleophile opens the triazinane ring. Another protonation of the nitrogen creates a good leaving group, and an internal nucleophilic attack by the sulfur atom and a loss of a proton yield ethanolamine (**5**) and thiadiazinane **2**.



Scheme 4.4 Proposed reaction mechanism for the formation of thiadiazinane 2.

5 The Reaction between Triazinane 1 and Excess HS^-

In Chapter 4, it was established that when triazinane **1** reacts with one equivalent of Na_2S at pH 10, thiadiazinane **2** and ethanolamine (**5**) were formed. It seemed reasonable to assume that **2** can react with a sulfide nucleophile in much the same way as **1**. However, the replacement of one ring nitrogen with sulfur should make at least two of the ring carbons less electrophilic, so **2** was expected to be less reactive than **1** towards nucleophilic substitution.

First, thiadiazinane **2** was reacted with one equivalent of NaHS. The products were analysed and isolated by the same methods used in the equimolar reaction of Chapter 4. The results are discussed in Section 5.1.

Then, the reaction between triazinane **1** and two equivalents of NaHS was analysed, and the findings were compared to the ones achieved in Chapter 4. This is described in Section 5.2. The isolation of the product and the analysis of the pure compound are presented in Sections 5.3 and 5.4, respectively.

Triazinane **1** was then reacted with up to five equivalents of HS^- in order to see if 1,3,5-trithiane (**4**) was formed. The results are presented in Section 5.5.

Finally, triazinane **1** was reacted with H_2S-gas and the findings were compared both with the ones from Chapter 4, and with ^1H NMR spectra from actual spent scavenger from a natural gas plant in the North Sea. These parts are treated in Sections 5.6 and 5.7.

All experimental details are given in Section 9.5.

5.1 Thiadiazinane 2 and NaHS

Isolated thiadiazinane **2** with a purity of about 75 %, the rest being dichloromethane and traces of 5-(2-hydroxyethyl)-1,3,5-dithiazinane (**3**), was reacted with one equivalent of NaHS at pH 10 and room temperature. The ^1H NMR spectra of the reaction mixture were recorded after 21 hours and again after two days. The latter spectrum is given in Figure 5.1.

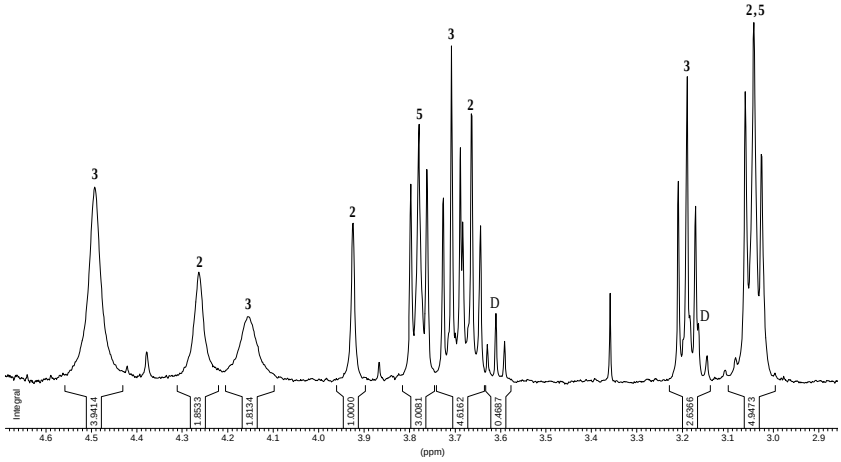
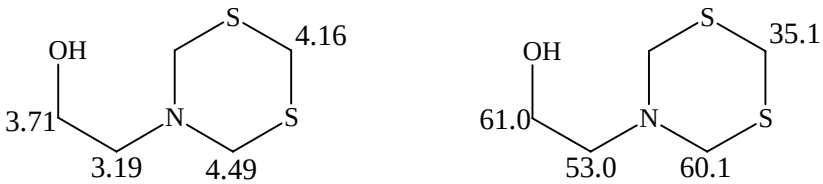


Figure 5.1 ^{1}H NMR spectrum of reaction mixture after equimolar reaction between 2 and HS^- (300 MHz, D_2O, pH 10).

From comparison of this NMR spectrum with the one in Figure 4.3, at least one new compound is formed, as the spectrum contains four new signals in addition to the signals from unreacted thiadiazinane **2**, ethanolamine (**5**) and the unknown compound D (Section 4.1.5). The new signals are two triplets at δ 3.19 and 3.71 ppm, and two broad singlets at δ 4.16 and 4.49 ppm. The intensity of the signals are 1:1:1:2, respectively, and their positions and shapes correspond well with those expected for 5-(2-hydroxyethyl)-1,3,5-dithiazinane (**3**). The structure of **3** is shown in Figure 5.2.

A ^{13}C NMR spectrum of the reaction mixture was recorded, and the spectrum contained four new signals: δ 35.1, 53.0, 60.1 and 61.0 ppm. These shifts correspond well with calculated ^{13}C NMR shift values for **3**.[11] The observed ^{1}H NMR and ^{13}C NMR shift values are assigned to dithiazinane **3** as shown in Figure 5.2.



a **b**

Figure 5.2 Dithiazinane 3 with observed ^{1}H (a) and ^{13}C (b) NMR shifts.

After 21 hours, 62 % of **2** had reacted and formed **3**. After two days, when the spectrum in Figure 5.1 was recorded, 68 % of **2** had reacted. Another ^1H NMR spectrum was recorded after seven days, and it was found that all of **2** had reacted. It is clear that the reaction between **2** and HS^- is considerably slower than the reaction between **1** and HS^-. Under the same conditions, only traces of **1** were left after 45 minutes of reaction with HS^- (Figure 4.1). This indicates that **2** is less reactive than **1**, which was expected considering the decrease in electronegativity of the ring carbons caused by the substitution of one ring nitrogen with a sulfur atom. From this it is also reasonable to assume that **2** is less susceptible to hydrolysis than **1**. Dithiazinane **3** should be even more stable and less reactive than **2**, following the same argument. The specific rates of hydrolysis or reactivities of thiadiazinane **2** or dithiazinane **3** were not determined.

5.2 Triazinane 1 and Two Equivalents of HS^-

Triazinane **1** was reacted with two equivalents of NaHS at room temperature and pH 10. The reaction was followed by ^1H NMR spectroscopy, which after one day showed that the same, new product was formed in this reaction as in the equimolar reaction between **2** and HS^- (Section 5.1). This product was assumed to be 5-(2-hydroxyethyl)-1,3,5-dithiazinane (**3**) from the NMR data. The spectra showed that even after four days, thiadiazinane **2** was present in the reaction mixture. This again indicated that thiadiazinane **2** reacts slower with HS^- than triazinane **1**.

5.3 Separation and Isolation of the Product

5.3.1 Liquid/Liquid Extraction

For the purpose of isolating the new product (**3**), a reaction mixture from the reaction between triazinane **1** and three equivalents of NaHS was used. As **2** and **3** are not very easily separated by liquid/liquid extraction (Section 4.2.1), the amount of **2** in the reaction mixture should be minimized. By using three equivalents of NaHS instead of two, a reaction mixture was obtained, in which what appeared to be dithiazinane **3** from the NMR data was by far the most dominant product. The other products were ethanolamine (**5**), thiadiazinane **2** and traces of the unknown compound D (Section 4.1.5). The reaction mixture was continuously extracted with dichloromethane. The solvent was removed by evaporation, and the resulting product was a yellow, viscous oil, similar to **1**

and **2** in physical appearance. A ^1H NMR spectrum in $CDCl_3$ showed that the obtained purity of **3** was 98 %, the only contaminant being dichloromethane.

5.3.2 Gas Chromatography

Isolated dithiazinane **3** was analysed by GC system number 2 (see Section 9.1.2). The result was a broad peak at 20.1 minutes in the chromatogram. Hence, **3** is the only compound that can be analysed by GC. However, as the other components of the reaction mixtures cannot be properly analysed by GC, this technique was not used to follow the reactions.

5.3.3 Short Path Distillation

As can be seen from Section 4.2.1, thiadiazinane **2** and dithiazinane **3** can be easily separated from the rest of the reaction mixture by water/dichloromethane extraction. However, if both compounds are present, separating them from each other by this method is slightly more difficult, as seen in Section 4.2.1. Short path distillation was attempted as another method of separating the two products from each other. A mixture of **2** and **3**, containing small amounts of **1** and **5**, was heated in the distillation apparatus. As the temperature was raised, the mixture gradually turned brown due to the decomposition of one or more of the components. No boiling was observed in the mixture at temperatures up to 200°C at 1.8×10^{-4} atm. A ^1H NMR spectrum was recorded after the attempted distillation, and apparently, most of the dithiazinane **3** was still intact. The signals from triazinane **1** and thiadiazinane **2** were barely visible in the spectrum and had decomposed. The relative amount of ethanolamine (**5**) had increased, indicating that **5** was one of the products of the decomposition. Some other, new products were also formed in small amounts during the experiment.

It was concluded that short path distillation was not a successful method for the purification of **2** and **3**.

5.4 Analysis of Dithiazinane 3

5.4.1 Mass Analysis

The isolation of the new product, assumed to be 5-(2-hydroxyethyl)-1,3,5-dithiazinane (**3**) from NMR data, made it possible to perform an elemental

analysis. Compound **3** has the molecular formula $C_5H_{11}NOS_2$. The result is presented along with the calculated composition in Table 5.1.[11]

***Table 5.1 Elemental analysis of dithiazinane** 3.*

	C (%)	**H (%)**	**N (%)**	**O (%)**	**S (%)**
Calculated	36.3	6.7	8.5	9.7	38.8
Found	35.7	6.5	8.4	-	37.2

The correspondence between calculated and observed values are significantly better for **3** than for **2** (see Table 4.4). This is explained by the fact that dithiazinane **3** is easier to isolate and has a higher purity. As for thiadiazinane **2**, the difference between the calculated and the observed values is attributed to the presence of dichloromethane in the product.

5.4.2 Low-Temperature ^{1}H NMR Spectra

In addition to ^{1}H and ^{13}C NMR data and elemental analysis, low temperature ^{1}H NMR spectroscopy was used to gain more information on the structure of the isolated product. ^{1}H NMR spectra of the isolated product were recorded at room temperature, -15 °C, -40 °C, -53 °C, -66 °C, and -79 °C. The spectra are shown in Figure 5.3.

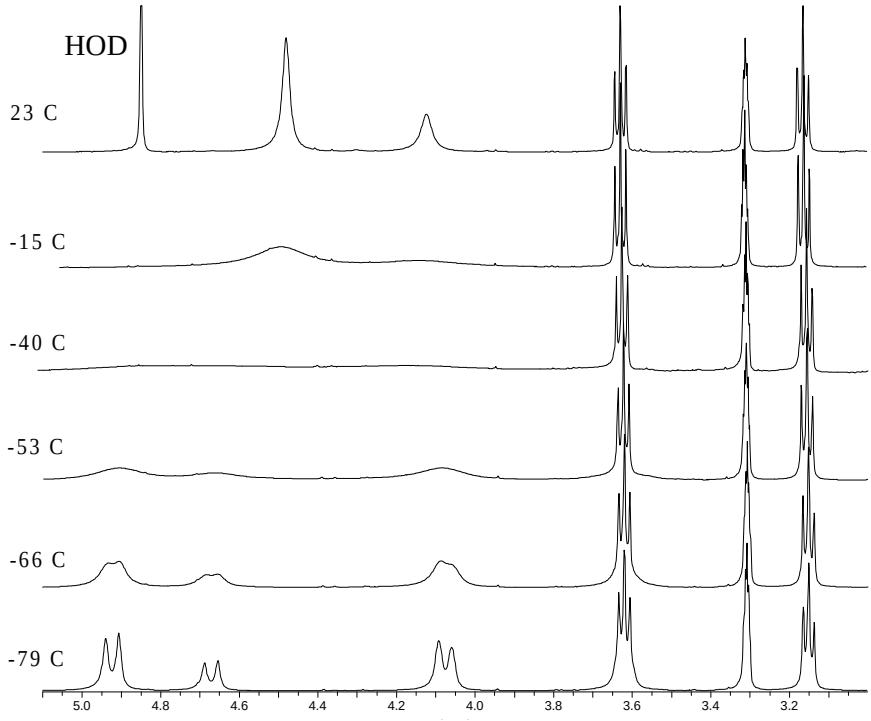


Figure 5.3 ^{1}H NMR spectra of dithiazinane** 3 **(400 MHz, CD_3OD).

The behaviour of the isolated compound behaved was very similar to thiadiazinane **2** when the temperature was lowered. As can be seen from the Figure 5.3, the two singlets that arise from the two types of ring protons are both splitted into two doublets at low temperatures, in accordance with the proposed structure of compound **3** as a cyclic compound. At -79 °C, the singlet originally located at δ 4.16 ppm is found as two doublets, one at δ 4.67 ppm with a coupling constant J = 13.5 Hz, and the other inside the triplet at δ 3.62 ppm (by comparison of the integrals). The singlet originally located at δ 4.49 ppm is found as two doublets of coupling constants J = 13.2 Hz, one at δ 4.92 ppm and one at δ 4.08 ppm.

When thiadiazinane **2** was analysed in the same manner (see Section 4.3.2), an additional splitting was observed. The triplet from the side chain methylene group in α-position to the nitrogen was splitted into two multiplets by the decrease in temperature. This was explained by the fact that the protons on the side chain in **2** are prochiral and magnetically non-equivalent. This was not

observed for **3**, which can be explained by the symmetry of the achiral dithiazinane molecule.

In conclusion, the low temperature ^1H NMR analyses strongly support the assignment of structure **3** as the isolated product.

5.4.3 IR Spectroscopy

Compound **3** was also analysed by IR spectroscopy. The characteristic absorptions are assigned as follows:[14] A strong O-H stretch absorption (3394 cm^{-1}) and a strong C-O stretch absorption (1059 cm^{-1}) were found in the spectrum, indicating that the isolated compound is an alcohol. A weak C-N stretch absorption (1195 cm^{-1}) showed that the compound also contains an amine moiety. Finally, a C-S stretch absorption (689 cm^{-1}) indicated the presence of a sulfur moiety. The C-H absorptions were found at 2915 cm^{-1} (stretch), 1429 cm^{-1} (scissors) and 728 cm^{-1} (rock).

In conclusion, the results from the IR analysis support that dithiazinane **3** is the isolated product.

5.5 Triazinane 1 and Large Excess of HS^-

The formation of thiadiazinane **2** from triazinane **1** and dithiazinane **3** from thiadiazinane **2** indicate that 1,3,5-trithiane (**4**) might be formed from dithiazinane **3** if enough HS^- is added. It was desirable to find out if **4** really can be formed during H_2S removal, mainly because **4** is likely to precipitate in water and cause problems in the pipelines.

5.5.1 Triazinane 1 and Three Equivalents of HS^-

Triazinane **1** was reacted with three equivalents of NaHS. After one week, only traces of the compounds **1** and **2** were found, and **3** and **5** were the main products of the reaction, in addition to small amounts of the unknown compound D from Section 4.1.5. No solids was formed.

5.5.2 Triazinane 1 and Five Equivalents of HS^-

The reaction between **1** and five equivalents of NaHS was performed, and the reaction followed by ^1H NMR. Again, no new products were observed in the spectrum, which after 2.5 hours contained thiadiazine **2**, dithiazinane **3** and

ethanolamine (**5**). However, after seven weeks, small amounts of a white solid had precipitated from the reaction mixture. A ^1H NMR analysis showed only the signals from **3**, **5** and the unknown compound D. The solid was insoluble in all the tried solvents (water, methanol, dichloromethane, DMSO and hexane), so a acceptable ^1H NMR spectrum of the compound(s) could not be obtained. IR analysis of the solid was not successful. The solid was put into an open flame, but the absence of the characteristic smell of SO_2 indicated that the white powder did not contain sulfur. The trithiane (**4**) is commercially available, and NMR analyses and melting point of the commercial compound are given in Appendix A. The white solid did not have a distinct melting point like **4**. A part of the solid apparently sublimed at 110 °C, and the rest gradually turned brown as the temperature was raised, indicating that decomposition took place.

In conclusion, the white solid formed in the reaction between **1** and five equivalents of HS^- was neither elemental sulfur nor 1,3,5-trithiane (**4**). The insolubility and the behaviour of the solid in the melting point apparatus indicated that the solid consisted of more than one polymer. The fact that the solid was not formed when **3** was mixed with excess Na_2S (Section 5.5.3) may be due to the lack of formaldehyde in this solution. As mentioned in Section 9.2, the synthesized **1** contains both water, ethanolamine (**5**) and formaldehyde. Formaldehyde can react with sulfides to form $(-CH_2-S-)_n$ type polymers, and sulfur-containing polymers cannot be excluded as products based only on the SO_2-test.

5.5.3 Dithiazinane 3 and Four Equivalents of HS^-

In order to see if new products were formed, dithiazinane **3** was reacted with two equivalents of Na_2S in an aqueous buffer-solution of pH 8.0, containing an internal standard. ^1H NMR spectra after 1 hour and 20 hours showed that the solution contained **3** only. Adjusting the pH to 6.0 for three hours, and to 2.0 for another 24 hours with the addition of another two equivalents of Na_2S made no change in the reaction mixture. All of **3** was still intact, an no solid was formed.

From these results, it was evident that dithiazinane **3** is a very stable compound. It does not react with Na_2S, nor does it hydrolyse at pH levels down to 2.0.

5.6 Triazinane 1 and Gaseous H_2S

In most of the experiments performed in this work, Na_2S or NaHS have been used as sulfide sources instead of gaseous H_2S. This was done both to achieve a better control of the stoichiometry of the reaction, and to avoid the hydrolysis by operating at higher pH. However, it was necessary to examine whether this in any way affected the outcome of the reaction in terms of the structures of the products. An experiment in which gaseous H_2S replaced the sulfide was performed.

Gaseous H_2S was bubbled through a 0.05M aqueous solution of triazinane **1** with acetonitrile as internal standard (IS) for 2.5 minutes. A ^1H NMR spectrum of the reaction mixture is showed in Figure 5.4.

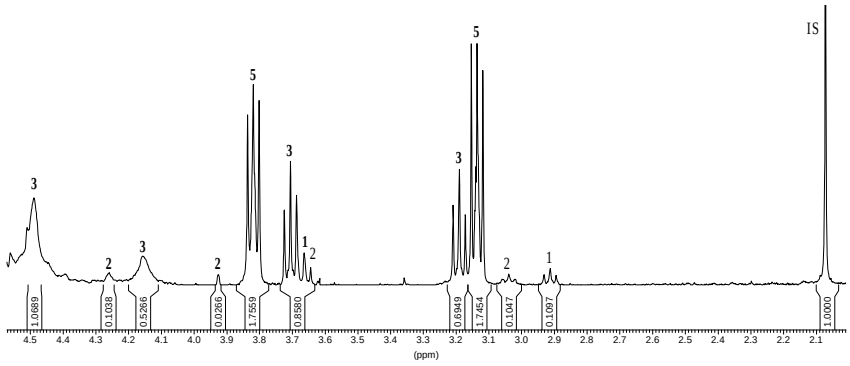


Figure 5.4 ^1H NMR spectrum of reaction mixture from the reaction between 1 and H_2S (300 MHz, D_2O).

As can be seen from the spectrum, the products formed from this reaction are identical to the ones formed when **1** is reacted with excess HS^-. In addition to the internal standard at δ 2.07 ppm, small amounts of unreacted **1** (the triplet at δ 2.91 ppm) and **2** (the triplet at δ 3.04 and the singlets at δ 3.93 and δ 4.26 ppm) are found. The main products, however, are **5** (the two triplets at δ 3.14 and 3.82 ppm) and **3** (the two triplets at δ 3.19 and 3.71 ppm, and the two singlets at δ 4.16 and 4.49 ppm). The integrals of the signals indicate that the reaction is nearly complete, and the fact that the amount of ethanolamine (**5**) present in the solution relative to **3** is about 2.5 indicates that some hydrolysis has taken place (the formation of one equivalent of **3** from one equivalent of **1** will release two equivalents of **5** - the rest is due to hydrolysis).

5.7 Spent Scavenger Solution

A sample of spent scavenger solution (a solution that originally consisted of 50 % **1** in water, *after* it had reacted with H_2S in the natural gas) was collected from one of the natural gas plants in the North Sea. The sample had a pH of 8.5. A ^1H NMR spectrum of the sample is shown in Figure 5.5.

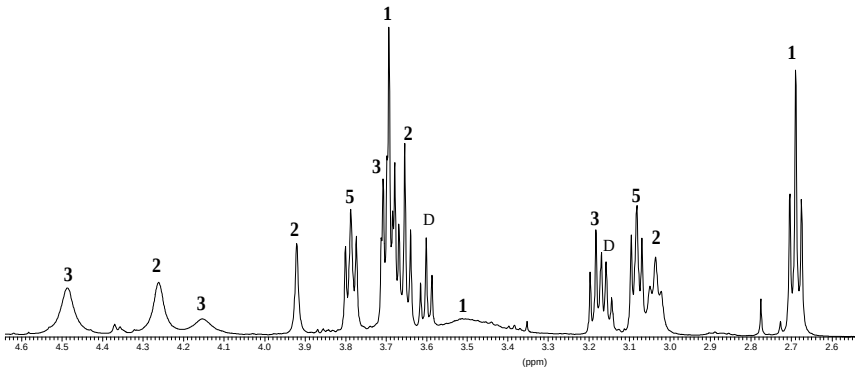


Figure 5.5 ^1H NMR spectrum of actual spent scavenger from the North Sea, with assignments (400 MHz, D_2O).

Comparisons of the spectrum in Figure 5.5 with the ones in Figures 5.1 and 5.4 show that the products formed in industrial scale H_2S scavenging are the same as the ones from small-scale laboratory experiments with excess Na_2S/NaHS or H_2S. The reaction mixture of Figure 5.5 consists of both **1**, **2**, **3** and **5** in addition to the unknown compound D (Section 4.1.5).

5.8 Conclusion

The reaction between the isolated thiadiazinane **2** from Chapter 4 and one equivalent of HS^- yielded ethanolamine (**5**) and a new product that was not observed in the equimolar reaction mixture. The same, new product was formed when triazinane **1** reacted with two equivalents of HS^-. This product was less polar than thiadiazinane **2**, but it had a similar structure according to the NMR data. The compound was successfully isolated by liquid/liquid extraction and identified as 5-(2-hydroxyethyl)-1,3,5-dithiazinane (**3**) by various NMR techniques, IR and elemental analysis.

Dithiazinane **3** is presumably formed from thiadiazinane **2** via the same mechanism that was proposed for the formation of **2** from triazinane **1**, shown in Scheme 4.4.

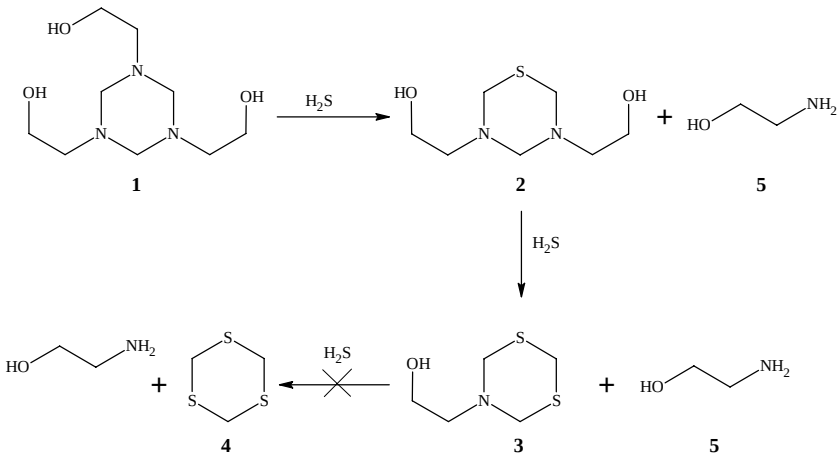
Upon addition of five equivalents of NaHS to **1**, no 1,3,5-trithiane (**4**) was formed, but the formation of **3** was complete. However, precipitation of a small amount of a white solid was observed. Analysis of the solid showed that it was not 1,3,5-trithiane (**4**). It was believed that the solid consisted of one or more polymers of the type $(-CH_2-S-)_n$.

Addition of two and four equivalents of NaHS to the isolated dithiazinane **3** gave no new products from ^1H NMR, and no formation of solids, even when the pH was lowered to 2.0. From this observation and the results of the attempted short path distillation of the products, it was concluded that dithiazinane **3** was significantly more stable and less reactive than thiadiazinane **2** and triazinane **1**. From the NMR results, it was also concluded that thiadiazinane **2** is less reactive than triazinane **1**, as most of **1** is converted into thiadiazinane **2** before any observable amount of dithiazinane **3** is formed.

When triazinane **1** was reacted with excess gaseous H_2S, the products formed were identical to the ones formed upon reaction between **1** and excess Na_2S or NaHS.

A ^1H NMR analysis of a solution of **1** after it had been used to remove H_2S from a natural gas stream in the North Sea showed that the same products are formed in industrial scale H_2S scavenging as in the laboratory experiments performed in this work.

Altogether, the structures of the reaction products from the removal of H_2S in the North Sea by triazinane **1** are considered to be firmly established. Depending on the relative concentrations of **1** and H_2S in the solution or gas stream, thiadiazinane **2**, dithiazinane **3** and ethanolamine (**5**) are formed in various relative amounts. The results are summarized in Scheme 5.1.



Scheme 5.1 Reaction scheme for the reaction between triazinane** 1 **and H_2S.

One of the products, 3,5-bis(2-hydroxyethyl)-1,3,5-thiadiazinane (**2**), have not been described in literature before.[13]

- Part II -

Determination of the Efficiency of Triazinane 1 in H_2S Removal

In the preceding chapters, the hydrolysis of triazinane **1** was investigated, both in terms of hydrolysis products and the rate of the hydrolysis. The qualitative aspect of the reaction between **1** and H_2S have been investigated thoroughly, and the main reaction products have been identified. A good understanding of what happens when **1** and H_2S react was achieved, and investigations of the reactivity of triazinane **1** as an H_2S scavenger could begin.

The overall chemical efficiency of **1** in H_2S removal depends on both the reactivity of **1** towards H_2S and its reactivity in competing reactions. In part I it was concluded that the hydrolysis of **1** was the only competing reaction of significance. Hence, to get a clear picture of the overall efficiency of triazinane **1** in H_2S removal, both the rate of hydrolysis of **1** and the rate of the reaction between **1** and H_2S had to be determined. The rate of hydrolysis was investigated and determined in Section 3.2. In Chapter 6, a method for determining the rate of reaction between triazinane **1** and H_2S is developed, and the reaction kinetics will be established.

6 The Rate of the Reaction between Triazinane 1 and H_2S

All experimental details are given in Section 9.6.

6.1 Kinetic Equations

As earlier mentioned (Section 4.4), experiments indicate that the reaction between triazinane **1** and HS^- is pH-dependent, and that activation of the triazinane in terms of protonation of the ring nitrogen is necessary to initiate the reaction. A reasonable assumption would be that the reaction rate is dependent on both the concentration of protonated **1** and the concentration of the sulfide nucleophile in the solution. From the plot in Figure 2.1, it is clear that in the pH area of interest - basically between 8 and 11 - H_2S is present almost exclusively as HS^-. This gives the following rate law, in which T stands for Triazinane (not necessarily just triazinane **1**, as other 1,3,5-triazinanes may react in the same way) and TH^+ for the protonated triazinane compound:

$$-\frac{d[T]}{dt} = k[TH^+][HS^-] \tag{6-1}$$

The concentration of protonated triazinane in the solution cannot easily be determined, and the acid constant of the compound must be taken into account. The equilibrium can be expressed as in Equation 6-2:

$$K_a = \frac{[T][H^+]}{[TH^+]} \tag{6-2}$$

Solved for $[TH^+]$, Equation 6-2 can be substituted into Equation 6-1. The result is a reaction rate that depends on the concentration of the triazinane compound, the pH and the concentration of HS^-. The new rate expression is

$$-\frac{d[T]}{dt} = k_3'[T][H^+][HS^-] \tag{6-3}$$

in which the new, apparent third order rate constant k_3' is

$$k_3' = k \cdot K_a^{-1} \tag{6-4}$$

Following all three concentrations of Equation 6-3 would require a very extensive analysis, so in order to determine the rate constant, simplifications must be made. If the reaction is run at constant pH, the concentration of protons is constant, and the new rate expression becomes

$$-\frac{d[T]}{dt} = k_2'[T][HS^-] \tag{6-5}$$

where

$$k_2' = k_3'[H^+] \tag{6-6}$$

The reaction rate now depends on the concentrations of both the triazinane and the sulfide nucleophile. To further simplify the expression, one of the concentrations must be kept constant. This can be achieved by running the reaction with large excess of one of the reactants. In this way, the reaction will cause only a negligible change in concentration of this reactant, and another constant is formed in the rate expression.

It had to be decided which of the concentrations should be followed during the reaction, and which should be used in large excess. For reasons described in the next sections, the concentration of the triazinane was chosen as the one to follow, and a large excess of HS^- was used. In doing so, the reaction becomes a pseudo first order reaction, and the rate expression becomes

$$-\frac{d[T]}{dt} = k_1'[T] \tag{6-7}$$

where

$$k_1' = k_2'[HS^-] \tag{6-8}$$

Integration of Equation 6-7 and insertion of the limiting condition that [T] = $[T]_0$ when t = 0 give

$$\ln \frac{[T]_0}{[T]} = k_1' t \tag{6-9}$$

In other words, a plot of the left side of Equation 6-9 against time should produce a straight line with a slope equal to k_1' if the original rate law and its modifications are all valid.

6.2 Method for Determination of Sulfide

In Equation 6-5, it had to be decided which concentration to follow. The concentration of sulfide would be a good choice for two reasons: The determination of the reaction kinetics would be independent of the type of scavenger investigated, and the preferred tool for following the concentration of sulfide - a sulfide-sensitive electrode - is more applicable for fast reactions.

The sulfide-sensitive electrode used in this experiment is only sensitive towards S^{2-}-ions. HS^--ions and H_2S are not detected. However, at a constant pH, the relative ratio between these species is constant, and the rate of reaction can be followed by measuring the concentration of S^{2-}. When using the electrode, a calibration curve must be made, in which an exponential relationship is found between $[S^{2-}]$ and the voltage registered by the electrode. The concentrations of the S^{2-}-standards were determined either by iodometric titration[16] or by titration with Pb^{2+} and the electrode[17].

6.2.1 The First Attempt

Initially, the reaction between a large excess (ten equivalents) of **1** relative to Na_2S was followed by taking out samples and analysing them with the electrode. The analysis was performed by first diluting the sample with specific

amounts of water and a buffered electrode stabilising solution[17] that raised the pH of the sample to 14. According to the producers of the electrode, all the sulfur in the solution is found exclusively as S^{2-} at this pH.[17] From Figure 2.1, this seems to be an erroneous assumption. Then, the voltage was recorded several times for each sample, and the voltage at the time of the dilution was found by extrapolation. The voltage was converted to $[S^{2-}]$ by the relationship from the calibration curve. In this way, the concentration of S^{2-} in the solution was followed, and a plot of $\ln([S^{2-}]_0/[S^{2-}])$ against time gave a straight line with a slope equal to the observed first order rate constant, $k_1' = 8.7\times10^{-3}$ s^{-1}. The experiment was reproduced, and the observed first order rate constant, $k_1' = 1.3\times10^{-2}$ s^{-1}.

With this procedure the uncertainties in the measurements were high, and measurements could not be performed as often as desired. Also, literature on the subject indicates that the reaction between **1** and H_2S was reversed at high pH levels,[8] making the use of the buffered electrode stabilising solution unfavourable.

In the two experiments performed, the pH decreased with half a unit as the reaction proceeded. Obviously, this seriously questions the reliability of the readings. However, as the pH in the two solutions decreased with the same rate, the pH in the two experiments were equal at all times, and the results could be compared. The variance of 44 % in the obtained value for k_1' showed that the reproducibility of this experiment was very poor. Another procedure had to be used.

6.2.2 The Second Attempt

Because of the poor reproducibility obtained in Section 6.2.1, it would be highly beneficial to record the sulfide concentration with the electrode directly in the reaction mixture. In this manner, many sources of error would be eliminated, e.g. the error in the volumes taken from the solution and the time that passed from the sample was taken out until the measurement was finished. The buffered stabilizing solution was not used, as the reaction between **1** and HS^- would not occur in a solution of pH 14. This procedure enabled measuring the sulfide concentration as often as desired. The reaction had to be run at constant pH in order to keep the ratio between $[S^{2-}]$ and $[HS^-]$ constant at all times. Hence, following $[S^{2-}]$ would give a clear picture of the overall reaction kinetics. The reactions were still run in large excess of triazinane **1**. The sulfide con-

centration was determined as the reaction proceeded, and plots were made assuming that the reaction was a pseudo first order reaction with respect to the sulfide concentration.

Straight lines were obtained, and the observed first order rate constant was found to be $k_1' = 1.6\times10^{-2}$ s^{-1}. The experiment was reproduced, giving a rate constant $k_1' = 1.6\times10^{-2}$ s^{-1}. Obviously, the reproducibility was improved when the electrode could be kept in the reaction mixture. However, without the stabilizing solution, the electrode might be more sensitive to small changes in the reaction procedure. A third experiment was performed, in which Na_2S substituted NaHS, which had been used in the previous two experiments as the sulfide source. This time, the found rate constant was $k_1' = 2.5\times10^{-2}$ s^{-1}. Some investigations were made in order to find the sources of error in these experiments, and they are presented in the next two sections.

6.2.3 The Calibration of the Electrode

During the work presented in the previous two sections, the electrode was calibrated several times. This was done by making standard solutions of S^{2-} in the same solvents and at the same pH as in the reaction that was to be analysed. The concentrations of the standards were verified by titration with I_2[18] or with Pb^{2+} and the electrode[17]. The standards were diluted in the same way as the samples in the experiments, and their voltage was recorded. From this, a calibration curve was made by plotting voltage (on a linear scale) against concentration (on a logarithmic scale), generating a straight line. The recorded voltages from the experiments were converted to sulfide concentrations using the calibration curve. However, initial sulfide concentration in the experiments often exceeded the expected value by more than 50 %. Iodometric titrations of some of the samples gave concentrations that were close to the expected values (see Section 6.2.4). Apparently, good calibration curves for the electrode were very difficult to obtain, and the reliability of the electrode had to be tested.

6.2.4 Reproducibility Tests of Sulfide Electrode

Based on the poor reproducibility of the previous experiments, it was desirable to see if a solution of S^{2-} in water would give stable readings over time. An aqueous solution of S^{2-} was analysed with the electrode directly in the solution, and the pH was held constant. No buffered stabilizing solution was used. The sulfide concentration decreased with time, and after 40 minutes at pH 10.0,

only half of the original amount of sulfide was left. At this pH, the amount of H_2S present in the solution was very small (see Figure 2.1), so the loss of sulfide as gaseous H_2S did not account for the large reduction in sulfide concentration with time. During the experiment, five iodometric titrations showed that the sulfide concentration was fairly constant. It was suspected that the electrode itself was inaccurate or inapplicable for these measurements.

The reproducibility of the electrode was tested by making three solutions, in which identical amounts of Na_2S were dissolved in identical volumes of the same buffer of pH 10.0. This should give three solutions with identical sulfide concentration. The three solutions were all analysed immediately after preparation. The deviation in the recorded voltages was up to 4.9 mV. As a rule of thumb, an increase in the voltage of 30 mV gives a ten-fold increase in concentration.[17] Hence, an increase of 5 mV corresponds to a 50 % increase in concentration. Iodometric titration of the three samples showed that the solutions had sulfide concentrations of 0.047, 0.047 and 0.048 M, respectively. Three days later, a new solution was made with the same concentration. The recorded voltage was up to 13.6 mV higher than the in other solutions. This corresponds to an increase of 100-200 % in concentration. Again, from iodometric titration, the solution had a sulfide concentration of 0.047 M. This illustrates not only the necessity to calibrate the electrode every day; the variations within the recordings done one a single day are also too large to comply with the need for a reliable and accurate determination of the sulfide concentration.

The unreliability of the measurements performed with the sulfide-sensitive electrode can be explained by the reactions being run mainly at pH 10.0. From Figure 2.1 it is clear that at this pH, the amount of S^{2-} is negligibly small compared to the amount of HS^-, which is the dominant species in the solution. Hence, the electrode is measuring very small concentrations of S^{2-} and the error of the method may become significant. Another possibility is that the performance of the electrode is somehow influenced by one or more of the other components in the mixture.

Because of the large uncertainty of the method in these experiments, it was concluded that the sulfide-sensitive electrode could not be used to examine the reaction kinetics of the reaction between triazinanes and HS^-.

6.2.5 Other Methods for Determination of Sulfide

Alternative methods for determination of [S^{2-}] were also tried. Taking out samples and titrating them with I_2 was tried,[18] but this rose the question of how to stop the reaction while the sample was titrated. An obvious alternative method would be to increase the pH until the reaction stopped (see Section 4.4), but since the addition of base have been reported to regenerate the triazinane with release of sulfide,[8] that method would be inapplicable for examining the kinetics of the reaction between **1** and HS^-.

In conclusion, the sulfide concentration in the reaction between triazinane **1** and HS^- could not accurately be determined by the methods employed in this work.

6.3 Method for Determination of Triazinane

Due to the lack of success in the determination of sulfide in the reaction mixture from the reaction between triazinane **1** and HS^-, other approaches would have to be considered. Based on the results obtained in Chapters 4 and 5, the reaction between triazinane **1** and HS^- could be followed in detail by ^1H NMR spectroscopy. The concentration of triazinane **1** could be determined from ^1H NMR spectroscopy by adding a known amount of an internal standard (IS) to the NMR sample. By comparing the integrals of the signals from **1** and the IS, the concentration of **1** could be determined.

Acetonitrile was used as IS in the kinetic experiments. A solution of one equivalent of the triazinane and the IS in D_2O was brought to the desired pH. Another solution of ten equivalents of Na_2S in D_2O was adjusted to the same pH. The concentrations were kept at a low level, so that the consumption of protons during the reaction did not cause a significant change in pH. At t = 0, the two solutions were mixed in the NMR tube, and ^1H NMR spectra were recorded with fixed intervals depending on the pH. Applied pH levels were 11.0, 10.5, and 10.0. For each experiment, twenty NMR spectra were recorded From each spectrum, the concentration of the triazinane was determined by integrating the signals of the triazinane and the IS.

Using the calculated concentrations of the triazinane, the left side of Equation 6-9 was plotted against time, and the pseudo first order rate constant k_1' was recorded as the slope of the linear relationship. From k_1' and the known con-

centration of HS^- (the known amount of Na_2S is assumed to be 100 % converted to HS^- at these pH levels, see Figure 2.1), k_2' for the pH level was calculated from Equation 6-8. This was done at three different pH levels, and a plot of the determined k_2' against the proton concentration gave a straight line, in accordance with Equation 6-6. The slope was equal to the rate constant k_3' of Equations 6-3 and 6-4. The rate constant of the original rate expression, k, can be calculated from k_3' and Equation 6-4 only when pK_a for the triazinane compound is known.

6.3.1 The Reactivity of Triazinane 1

The method described in Section 6.3 was used to determine the reaction kinetics of the reaction between triazinane **1** and HS^-. The experiment was performed at pH 11.0, 10.5 and 10.0. An example of a plot of Equation 6-9 is shown in Figure 6.1.

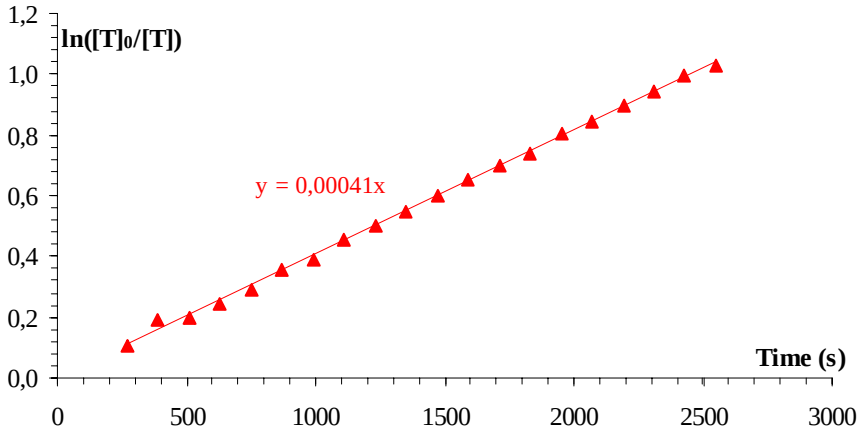


Figure 6.1 Plot of $ln([T]_0/[T])$ vs. time for triazinane *1* (pH 11.0).

The near-perfect linear relationship found in Figure 6.1 strongly indicated that Equation 6-9 was valid throughout the experiment, and that the requirements such as constant pH and large excess of HS^- were fulfilled. Linear regression of the data points yielded a regression line with a slope equal to the observed first order rate constant k_1'. In exactly the same way, k_1' was determined at pH 10.5 and 10.0. Then, for the three experiments, k_2' was calculated from $[HS^-]$ and Equation 6-8. A plot of the calculated values for k_2' versus $[H^+]$ resulted in

a straight line with a slope equal to k_3' in accordance with Equation 6-6. The plot is shown in Figure 6.2, and the kinetic results for the reaction between triazinane **1** and HS^- are presented in Table 6.1.

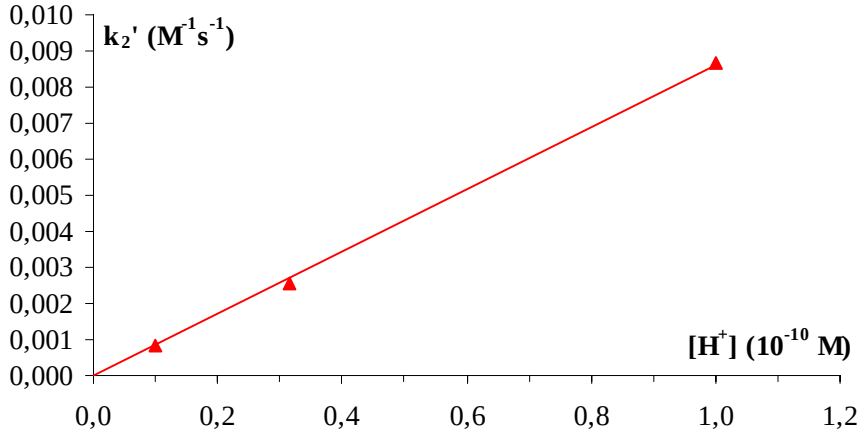


Figure 6.2 Plot of k_2' versus $[H^+]$ for triazinane *1*.

Table 6.1 Kinetic results for the reaction between triazinane *1* and HS^-.

pH	$[H^+]$	k_1' 10^{-3} (s^{-1})	$[HS^-]$ (M)	k_2' (10^{-3} $M^{-1}s^{-1}$)	k_3' (10^{7} $M^{-2}s^{-1}$)
11.0	1.0×10^{-11}	0.408 ± 0.001	0.48 ± 0.01	0.85 ± 0.02	
10.5	3.2×10^{-11}	1.28 ± 0.01	0.48 ± 0.01	2.7 ± 0.1	9.1 ± 0.2
10.0	1.0×10^{-10}	4.32 ± 0.04	0.48 ± 0.01	9.0 ± 0.2	

The rate constant k from the original rate expression (Equation 6-1) can be calculated from k_3' when the acid constant K_a of **1** is known. Such information was not found in the literature for triazinane **1**. However, if the compounds with which **1** will be compared can be assumed to have similar pK_a values to triazinane **1**, these results will still give a good indication of which compound reacts faster with H_2S.

Uncertainties in k_1' and k_3' were determined by linear regression, and they were less than 1 % for these measurements. The uncertainties in k_2' were calculated from Equation B-6 in Appendix B and were up to 6 %. The accuracy of the results was good and indicated that the method should give reproducible results.

6.3.2 Applicability of the Method

The method described in Section 6.3 gave good and accurate results when applied to the reaction between triazinane **1** and HS^-. Given the right rate expression, some modifications such as constant pH and concentration of one of the reactants, and necessary chemical data like the pK_a of the compound to be tested, the reaction kinetics can be firmly established. The kinetics form a basis upon which the compound can be compared with other compounds in terms of efficiency in H_2S removal. In principle, any compound can be analysed this way. However, there are some limitations:

- The compound must be identifiable by ^1H NMR spectroscopy. Chemical shifts, coupling constants and their change with the reaction conditions.
- All side-reactions must have been identified and their impact on the reaction with H_2S must be known. If possible, they should be avoided. One example is the hydrolysis of triazinane **1**.
- Upon reaction of the compound with H_2S, a new compound must be formed with ^1H NMR signals that are distinguishable from the signals of the original compound.

6.4 Conclusion

A method was developed, in which the efficiency of a compound as an H_2S scavenger can be determined in terms of reaction kinetics. The technique uses an internal standard in ^1H NMR spectroscopy and is general. Most organic compounds can be analysed using this method. An important requirement, however, is that the reaction products of the compound with H_2S must form a new compound with ^1H NMR shifts that are distinguishable from the signals of the original compound.

The NMR method was used to determine the rate constants of the reaction between 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane (**1**) and HS^-. The rate expression was found to be

$$-\frac{d[T]}{dt} = k[TH^+][HS^-]$$

and the rate constant

$$k = K_a \cdot 9.1 \times 10^7 \, M^{-2} s^{-1}$$

In sum, the use of internal standard in ^{1}H NMR is a good method for determining the rate of the reaction between triazinane **1** and HS^-. Other compounds can be analysed in the same way, and the results can be compared to the results for triazinane **1**. Thus, this method was preferred as the method for comparing the efficiency of **1** with that of other potential scavengers.

- Part III -

Suggestion, Synthesis and Testing of Potential New H_2S-Scavengers

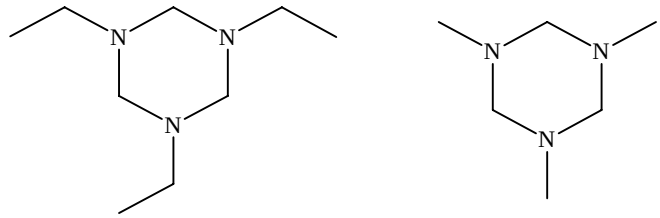
With the method for testing the efficiency of various scavengers developed in Part II of this work, it was possible to determine the efficiency of other compounds in H_2S removal. The potential scavengers to be tested had to fulfil all requirements stated in Section 6.3.2. When the reaction kinetics had been established, the results could be compared with the results obtained for triazinane **1** (Chapter 6).

As a first approach, compounds with structures and properties similar to triazinane **1** were tested. Other 1,3,5-triazinanes might be more reactive towards H_2S, or less susceptible to hydrolysis. In Chapter 7, other triazinanes are suggested and tested.

Another class of compounds that has been considered as H_2S scavengers is formaldehyde and derivatives thereof. Formaldehyde itself is reactive towards H_2S and was used in H_2S removal for many years.[18] It has now been replaced by other solutions, due to the toxic properties of formaldehyde. In this work, an oxolane and trimers and tetramers of formaldehyde have been analysed. The results are presented in Chapter 8.

7 Stability and Reactivity of Other 1,3,5-Triazinanes

Having developed the methods for determining the stability (Section 3.2) and reactivity (Section 6.3) of triazinane **1** in H_2S removal, other compounds can be tested and compared with **1**. It is likely that 1,3,5-triazinanes with other substituents than the hydroxyethyl-substituents of triazinane **1** will also react with HS^-. 1,3,5-triethyl-1,3,5-triazinane (**8**) and 1,3,5-trimethyl-1,3,5-triazinane (**9**) were analysed in order to see the potential effect of removing the hydroxyl group and decreasing the chain length. Their structures are shown in Figure 7.1.

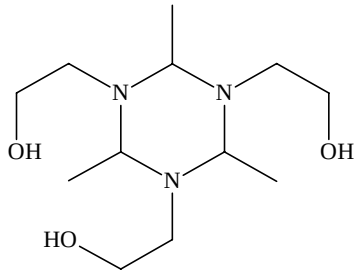


8 **9**

Figure 7.1 Structures of triazinane compounds** 8 **and** 9**.

The analysis of triazinane **8** is presented in Section 7.1, whereas the analysis of triazinane **9** is discussed in Section 7.2.

Another part of the triazinane molecule that can be modified is the site of the nucleophilic attack. Substituents in this position will influence the rate of reaction with nucleophiles, as well as the stability of the molecule. An electron-withdrawing group in this position would make the ring carbon even more electrophilic and reactive, but if the substituent is large, steric hindrance would lower the reactivity against nucleophilic attack. The simplest substituent would be a methyl group. Alkyl groups are weakly electron-donating and are not expected to increase the reactivity of the molecule, but they might improve the stability of the triazinane. Synthesising such a molecule would also give a good indication of the simplicity of the synthesis of 2,4,6-substituted 1,3,5-triazinanes. Therefore, the synthesis and testing of 2,4,6-trimethyl-1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane (**10**) would be useful. Its structure is shown in Figure 7.2.



10

***Figure 7.2 Structure of triazinane compound** 10.*

The attempted synthesis and analysis of triazinane **10** is presented in Section 7.3.

The results of the analyses of the 1,3,5-triazinanes are compared with each other and with the results for triazinane **1** in Section 7.4.

All experimental details are given in Section 9.7.

7.1 1,3,5-Triethyl-1,3,5-triazinane

An aqueous solution of 1,3,5-triethyl-1,3,5-triazinane (**8**) was provided by Dynea Oil Field Chemicals. Initial ^{1}H NMR and ^{13}C NMR analyses of the compound were performed and the NMR data are presented in the experimental section (Section 9.7.1) and in Appendix A.

7.1.1 Rate of Hydrolysis

If triazinane **8** hydrolyses in the same manner as triazinane **1**, ethylamine (**11**) and formaldehyde dihydrate is expected to be found in the hydrolysis mixture. An aqueous solution of **8** was adjusted to pH 10.0. A ^{1}H NMR spectrum of the hydrolysis mixture after one hour is shown in Figure 7.3.

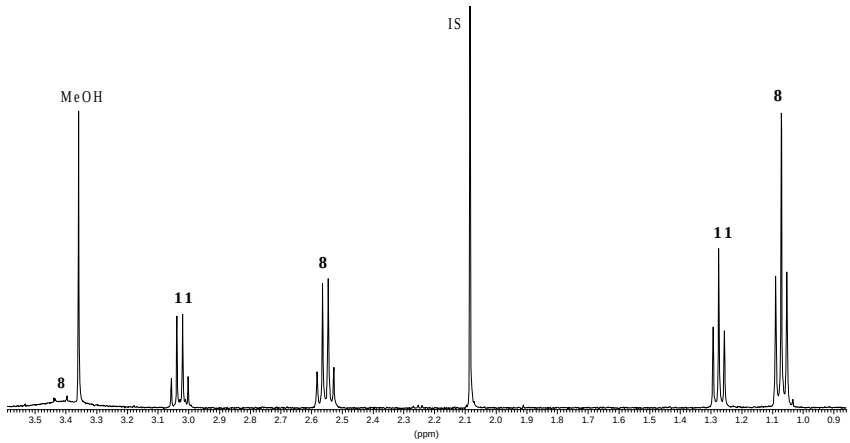


Figure 7.3 ^{1}H NMR spectrum, hydrolysis of triazinane** 8 **(400 MHz, D_2O, pH 10.0).

In the spectrum, triazinane **8** is found as a triplet at δ 1.07 ppm, a quartet at δ 2.56 ppm, and a broad, barely visible signal at δ 3.4 ppm. The triplet at δ 1.27 ppm and the quartet at δ 3.03 ppm are assigned to ethylamine (**11**), which is one of the products of the hydrolysis. Based on the results for triazinane **1**, it is assumed that formaldehyde is also formed, and that its signal is located inside the large water signal at δ 4.8 ppm. The singlet at δ 2.08 ppm is ascribed to acetonitrile, the IS used in the kinetic experiment. The singlet at δ 3.36 ppm is from methanol, which is present in the triazinane solution.

The stability of **8** was examined by determining the rate of the hydrolysis of the compound. The method was identical to the method used for triazinane **1**, described in Section 3.2.

A solution of triazinane **8** and the IS in D_2O and a D_2O-buffer of the desired pH was mixed in an NMR-tube. ^{1}H NMR-spectra were recorded at room temperature with fixed intervals, and the concentration of **8** was determined from each of them. The observed rate constants k_{obs} were determined from plots of $\ln([T]_0/[T])$ versus time, equivalent to the one in Figure 3.2. In accordance with Equation 3-3, k_1 and k_2 of the rate expression in Equation 3-1 were calculated from a plot of k_{obs} versus proton concentration at three different pH levels. The plot was equivalent to the one in Figure 3.3. The results are presented in Table 7.1.

Table 7.1 Rate constants and $t_{½}$ for the hydrolysis of triazinane 8, 22 °C.

pH	$[H^+]$ (M)	k_{obs} (10^{-4} s^{-1})	$t_{½}$ (10^2 s)	k_1 (10^{-5} s^{-1})	k_2 (10^5 $M^{-1}s^{-1}$)
10.0	1.0×10^{-10}	1.15 ± 0.01	60.3 ± 0.1		
9.0	1.0×10^{-9}	7.9 ± 0.1	8.8 ± 0.1	7 ± 3	6.9 ± 0.1
8.0	1.0×10^{-8}	69.7 ± 0.6	0.994 ± 0.009		

The uncertainties in the rate constants and half-lives were determined by exactly the same procedures as for triazinane **1** (see Section 3.2.2). For k_{obs} and k_2, only minor uncertainties (approximately 1 % each) were found. The half-lives depend only on k_{obs}, and the uncertainties in these values were also close to 1 %. As for triazinane **1**, the value for k_1 suffered from a larger error, approximately 43 %.

The calculated rate constants and half-lives are very accurate when pH is at a level where k_1 can be neglected. At pH close to 9 and above, k_1 becomes significant and the accuracy of the results decreases.

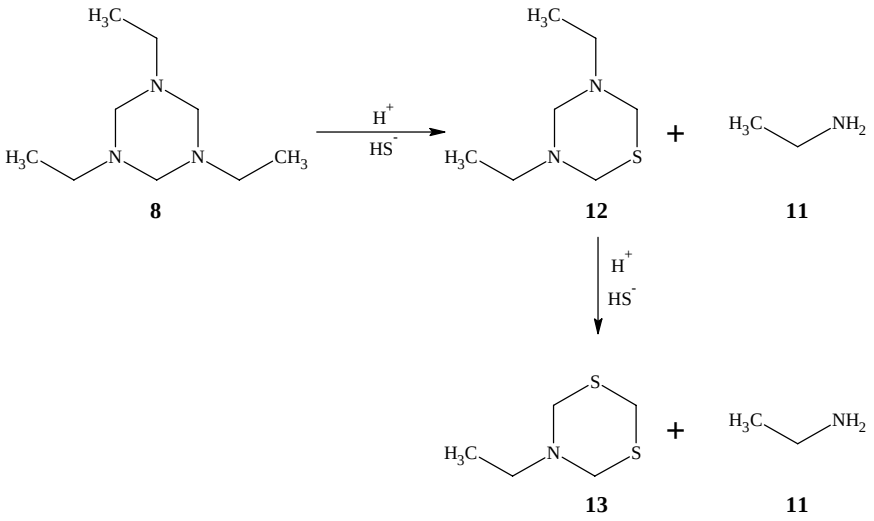
These results are compared with the corresponding results for triazinanes **1** and **9** in Section 7.4.

7.1.2 Reaction Products with H_2S

When the stability of triazinane **8** had been determined, the products of its reaction with H_2S had to be identified, in order to examine the efficiency of **8** in H_2S removal by the ^1H NMR method developed in Section 6.3.

Triazinane **8** was reacted with two equivalents of NaHS at pH 10.0. By analogy to the reaction of **1** with HS^- at the same conditions, the formation of 3,5-diethyl-1,3,5-thiadiazinane (**12**) and 5-ethyl-1,3,5-dithiazinane (**13**), in addition to ethylamine (**11**), is expected. The reaction is assumed to proceed as indicated in Scheme 7.1.

.



Scheme 7.1 Expected course of reaction between triazinane** 8 **and HS^-.

A ^{1}H NMR spectrum of the reaction mixture is shown in Figure 7.4.

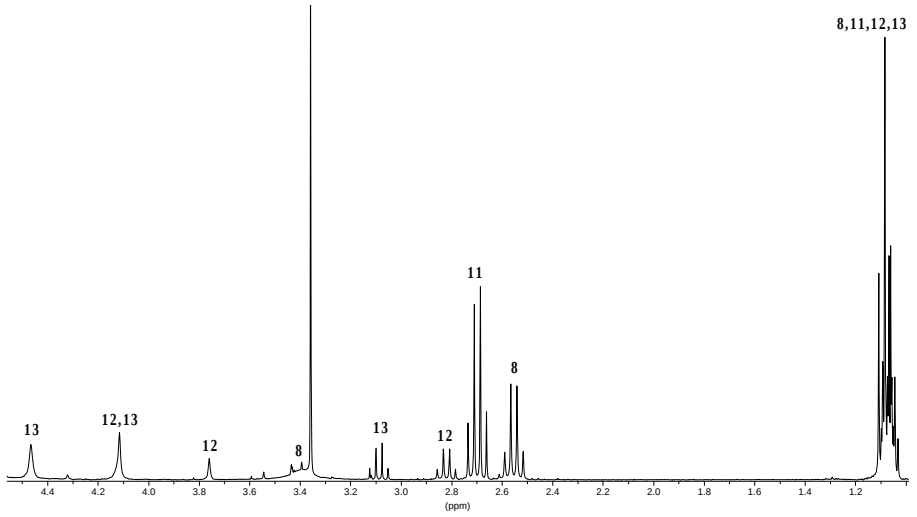


Figure 7.4 ^{1}H NMR spectrum of reaction mixture (300 MHz, D_2O).

The neighbouring methylene groups in triazinane **8** and ethylamine (**11**) are found as the quartets at δ 2.55 and 2.70 ppm, respectively. The multiplet at δ 1.04-1.11 ppm contains the triplets from their respective methyl groups. The rest of the signals, including two triplets inside the multiplet at δ 1.04-1.11 ppm, are assigned to new products. The three broad signals at δ 3.76, 4.12 and

4.66 ppm are within the shift range expected for thiadiazinanes and dithiazinanes.

In addition, the reaction mixture was analysed by ^{13}C NMR, HETCOR, ^{1}H,^{1}H COSY and 2D NOESY. All NMR data, and assignments to the structures in Scheme 7.1, are given in Table 7.2.

Table 7.2 Experimental NMR data for reaction between 8 and HS^- (300 MHz, D_2O).

^{1}H NMR δ (ppm)	**Multi-plicity**	***J* (Hz)**	**^{13}C NMR δ (ppm)**	**^{1}H NMR coupling to δ (ppm)**	**2D NOESY with δ (ppm)**	**Compound number**
1.04-1.11	t t t t	- - - -	11.2 11.2 11.7 16.5	2.70 3.09 2.82 2.55	all other signals	**11** **13** **12** **8**
2.55	q	7.3	46.7	1.04-1.11	1.04-1.11 3.40	**8**
2.70	q	7.2-7.3	35.6	1.04-1.11	1.04-1.11	**11**
2.82	q	7.2-7.3	46.9	1.04-1.11	1.04-1.11 3.76 4.12	**12**
3.09	q	7.3-7.4	42.7	1.04-1.11	1.04-1.11 4.66	**13**
3.4	s, br.	-	71.7	-	1.04-1.11 2.55	**8**
3.76	s	-	71.7	-	1.04-1.11 2.82 4.12	**12**
4.12	s+s [a]	-	32.5+54.2	-	1.04-1.11 2.82 3.76	**12+13**
4.66	s	-	56.1	-	1.04-1.11 3.09	**13**

a. Although this signal seems to contain only one singlet from the 2D NOESY experiment, the integral of the signal indicates that the missing singlet in compound **13** is also a part of the signal.

A control experiment was performed, in which **8** was reacted with one equivalent of NaHS. With this stoichiometry, only **12** and ethylamine (**11**) was formed. The experiment supported the assignments of compound **12** as 3,5-diethyl-1,3,5-thiadiazinane and **13** as 5-ethyl-1,3,5-dithiazinane.

In the reaction mixture with two equivalents of HS^-, a non-aqueous phase was observed after four weeks. This indicated that one of the products had poor

water-solubility. A ^{1}H NMR spectrum of the non-aqueous layer showed that it contained compounds **12** and **13** in relative amounts of 1:7. At the same time, a ^{1}H NMR spectrum of the remaining aqueous phase showed that **12** was present, as well as traces of **13**. This observation corresponded well with the assignment of compounds **12** and **13**, as substitution of a ring nitrogen with sulfur makes the molecule less polar. Solubility tests of commercially available 1,3,5-trithiane (**4**) showed that it has poor solubility in water. Thiadiazinane **12** is more polar, and therefore more soluble in water, but it is also soluble in the liquid **13** and was thus found in both phases. No attempt to further isolate the products was made.

From the NMR experiments and the experience with the reaction of triazinane **1** with HS^-, it was reasonable to assume that triazinane **8** reacted with H_2S to form the products **11**, **12** and **13**, as shown in Scheme 7.1.

As for triazinane **1**, it was timely to see if the same products were formed when **8** reacted with H_2S. Gaseous H_2S was bubbled through an aqueous solution of **8**. After 10 minutes, a ^{1}H NMR spectrum was recorded, and by comparison with the data in Table 7.2 it was concluded that dithiazinane **13** and ethylamine (**11**) had been formed. Neither triazinane **8** nor thiadiazinane **12** was found, indicating that the reaction was complete.

7.1.3 Rate of Reaction with H_2S

When the products of the reaction between **8** and HS^- had been identified and all the signals in the ^{1}H NMR spectrum had been assigned, the rate of the reaction was examined by the method described in Section 6.3. Triazinane **8** was reacted with ten equivalents of Na_2S, and the reaction was followed by ^{1}H NMR spectroscopy at room temperature. The rate of reaction was examined at pH 11.0, 10.5 and 10.0, and the findings are given in Table 7.3.

Table 7.3 Kinetic results for the reaction between triazinane** 8 **and HS$^-$, 22 °C.

pH	**[H^+]**	**k_1' 10^{-3} (s^{-1})**	**[HS^-] (M)**	**k_2' (10^{-3} $M^{-1}s^{-1}$)**	**k_3' (10^7 $M^{-2}s^{-1}$)**
11.0	1.0×10^{-11}	0.208 ± 0.002	0.48 ± 0.01	0.43 ± 0.01	
10.5	3.2×10^{-11}	0.612 ± 0.006	0.48 ± 0.01	1.3 ± 0.1	5.6 ± 0.4
10.0	1.0×10^{-10}	2.56 ± 0.03	0.48 ± 0.01	5.3 ± 0.1	

The observed first order rate constant k_1' was determined from plots of $\ln([T]_0/[T])$ against time, equivalent to the plot in Figure 6.1. The uncertainty of this value was estimated from linear regression of the data. The rate constants k_2' were calculated from k_1', $[HS^-]$ and Equation 6-8. The uncertainties in k_2' were up to 8 % from Equation B-6 in Appendix B. Finally, k_3' was determined from a plot of k_2' against $[H^+]$ for the three experiments. The uncertainty of k_3' was found from linear regression of the experimental data points. The accuracy of the results were acceptable, as the uncertainty of the rate constant k_3' was found to be 7 %.

7.2 1,3,5-Trimethyl-1,3,5-triazinane

In order to establish the effect of a smaller alkyl substituent on the triazinane ring, both the stability and reactivity of 1,3,5-trimethyl-1,3,5-triazinane (**9**) in H_2S-removal had to be determined. An aqueous solution of **9** was provided by Dynea Oil Field Chemicals.

7.2.1 Rate of Hydrolysis

Based on the results for triazinanes **1** and **8**, the hydrolysis of triazinane **9** was expected to yield hydrated formaldehyde and methylamine (**14**). An aqueous solution of **9** was kept at pH 10.0 for one hour. A ^{1}H NMR spectrum of the hydrolysis mixture is shown in Figure 7.5.

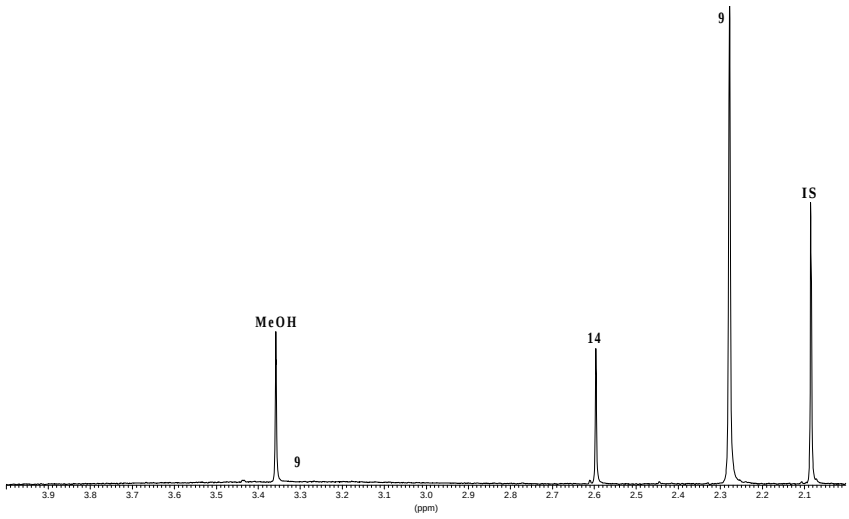


Figure 7.5 ^{1}H NMR spectrum, hydrolysis of triazinane 9 (400 MHz, D_2O, pH 10.0).

The singlet at δ 2.28 ppm was assigned to 1,3,5-trimethyl-1,3,5-triazinane (**9**) by comparison with ^{1}H NMR spectra of the solution before the hydrolysis was started (see Appendix B). The ring protons in **9** gave a signal that is barely visible in the ^{1}H NMR spectrum (δ 3.0-3.7 ppm). As for the triazinanes **1** and **8**, the broadness of the signal is due to ring-flip of the triazinane ring. The singlet at δ 2.08 ppm originated from the internal standard (IS). Methanol was present in the aqueous solution of **9** and was found in the spectrum as the singlet at δ 3.36 ppm. The integral of the singlet at δ 2.60 ppm increased as the integral of the triazinane signal decreased, and the former signal was thus assigned to methylamine (**14**).

The rate of hydrolysis of triazinane **9** was determined by using the same procedure as for triazinanes **1** and **8**. The results are shown in Table 7.4.

Table 7.4 Rate constants and $t_{½}$ for the hydrolysis of triazinane** 9**, 22 °C .

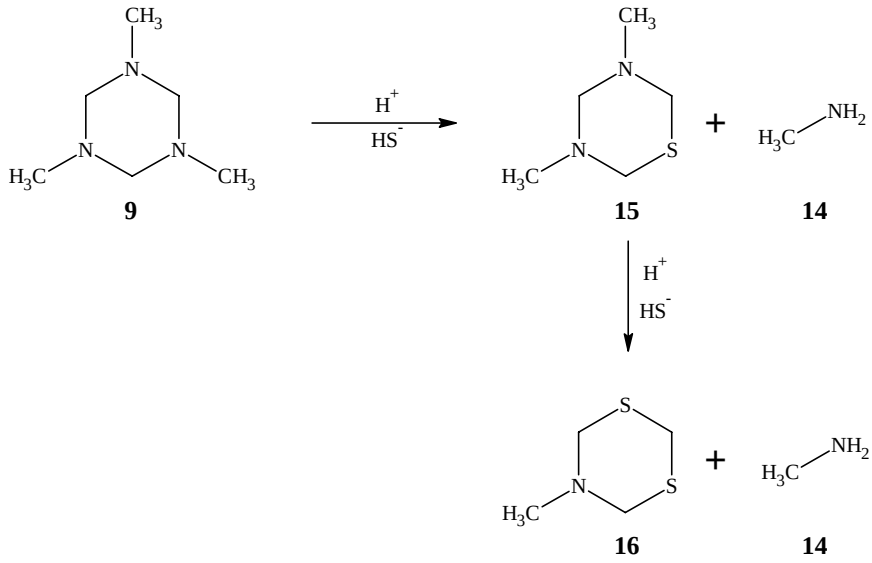
pH	$[H^+]$ (M)	k_{obs} (10^{-4} s^{-1})	$t_{½}$ (10^4 s)	k_1 (10^{-5} s^{-1})	k_2 (10^4 $M^{-1}s^{-1}$)
10.0	1.0×10^{-10}	0.05 ± 0.01	14 ± 3	3 ± 4	5.8 ± 0.3
9.0	1.0×10^{-9}	0.55 ± 0.01	1.26 ± 0.02		
8.0	1.0×10^{-8}	6.83 ± 0.02	0.102 ± 0.001		
7.5	3.2×10^{-8}	18.2 ± 0.1	0.0381 ± 0.0002		

The uncertainties of the results were calculated as explained in Section 7.1.1. At pH 10.0, the hydrolysis of **9** was very slow, only minor changes were observed in the ^{1}H NMR spectra. Hence, random variatons in the integrals became significant, and the uncertainty in k_{obs} at this pH was as large as 20 %. This is reflected in the calculated half-life of **9** at this pH, which has an uncertainty of 21 %. In order to increase the overall accuracy of the results, a fourth experiment was performed at pH 7.5. The observed rate constants and half-lives of the latter three experiments all had uncertainties of less than 2 %. Again, the uncertainty in k_1 was very large, in fact more than 130 %. The uncertainty in k_2 was only about 5 %. The accuracy of the results are acceptable at pH levels where k_1 can be neglected, in this case when pH is lower than 8. Above this pH, the k_1 term of Equation 3-1 becomes significant, and the reliability of the predictions diminishes.

The results of these experiments are compared with the corresponding results for triazinanes **1** and **8** in Section 7.4.

7.2.2 Reaction Products with H_2S

As for triazinane **8**, the first step towards determining the reactivity of triazinane **9** with HS^- was to identify the reaction products. For this purpose, **9** was reacted with two equivalents of NaHS at pH 10.0. Triazinane **9** is expected to react in the same way as triazinanes **1** and **8**, with the formation of 3,5-dimethyl-1,3,5-thiadiazinane (**15**) and 5-methyl-1,3,5-dithiazinane (**16**), in addition to methylamine (**14**). The reaction is showed in Scheme 7.2.



Scheme 7.2 Expected course of reaction between triazinane** 9 **and HS^-.

The reaction was very slow; after three days, precipitation of white, needle-shaped crystals was observed. Figure 7.6 shows a ^1H NMR spectrum of the remaining reaction mixture.

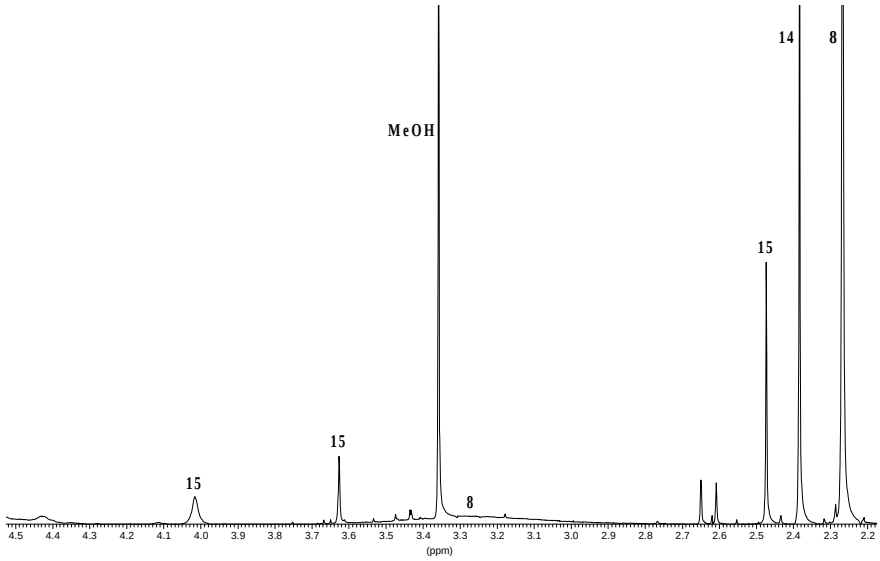


Figure 7.6 ^{1}H NMR spectrum of the reaction between 9 and HS^- (300 MHz, D_2O).

The reaction mixture was also analysed by ^{13}C NMR, HETCOR and 2D NOESY. The NMR data is presented in Table 7.5.

Table 7.5 Experimental NMR data for reaction between 9 and HS^- (400 MHz, D_2O).

^{1}H NMR δ (ppm)	**Multi-plicity**	**^{13}C NMR δ (ppm)**	**2D NOESY with δ (ppm)**	**Compound number**
2.27	s	41.9	3.25	**9**
2.38	s	28.8	-	**14**
2.47	s	43.1	3.65 4.02	**15**
3.25	s, br.	77.5	2.27	**9**
3.65	s	77.6	2.55 4.02	**15**
4.02	s	58.5	2.55 3.65	**15**

The crystals were isolated and their melting point was 63.5-65.0°C. The results from the ^{1}H and ^{13}C NMR analyses of the crystals are shown in Table 7.6.

Table 7.6 Experimental NMR data for isolated crystals (400 MHz, $CDCl_3$).

^{1}H NMR δ (ppm)	**Multi-plicity**	**^{13}C NMR δ (ppm)**	**Compound number**
2.69	s	60.0	**16**
4.09	s	37.6	**16**
4.42	s	34.4	**16**

Traces of the signals in Table 7.6 were also observed in the ^{1}H and ^{13}C NMR spectra of the reaction mixture. The proposed structure of compound **16**, 5-methyl-1,3,5-dithiazinane, corresponded well with the findings, as the dithiazinane compound is expected to be the least water-soluble of the components in the reaction mixture. The crystals were analysed by electron impact mass spectroscopy (EIMS), and the molecular ion $M^{+\cdot}$ was found at m/z 135.1. The presence of an M+2 peak with an intensity of 8.8 % of the $M^{+\cdot}$ intensity is consistent with the molecule containing two sulfur atoms. High resolution MS gave an exact molar mass of 135.01771 for the molecule. The calculated[19] mass for dithiazinane **16** ($C_4H_9NS_2$) is 135.01765. The deviation between the calculated and observed molecular mass was less than 0.5 ppm. Consequently, the MS results strongly supported the results from the NMR analyses, and the formed crystals were identified as 5-methyl-1,3,5-dithiazinane (**16**).

Again, it was essential to find out if the same products are formed when **9** reacts with gaseous H_2S. The gas was bubbled through an aqueous solution of **9** for 23 minutes. A ^{1}H NMR spectrum was recorded, showing that all of the starting material had disappeared, while methylamine (**14**) and dithiazinane **16** had been formed. This was consistent with the results for triazinanes **1** and **8**, which also formed the corresponding dithiazinane compound upon reaction with H_2S.

7.2.3 Rate of Reaction with H_2S

The rate of the reaction between triazinane **9** and HS^- was studied by ^{1}H NMR spectroscopy. The procedure was identical to the one used with triazinane **1** (Section 6.3). Triazinane **9** was reacted with ten equivalents of HS^-, and the concentration of **9** was followed by ^{1}H NMR spectroscopy at room temperature. As with triazinanes **1** and **8**, the rate constants k_1', k_2' and k_3' were deter-

mined by Equations 6-6, 6-8 and 6-9, and by plots equivalent to the ones in Figures 6.1 and 6.2. The results are given in Table 7.7.

Table 7.7 Kinetic results for the reaction between triazinane** 9 **and HS^-, 22 °C.

pH	$[H^+]$	k_1' (10^{-3} s^{-1})	$[HS^-]$ (M)	k_2' (10^{-3} $M^{-1}s^{-1}$)	k_3' (10^{7} $M^{-2}s^{-1}$)
11.0	1.0×10^{-11}	0.014 ± 0.003	0.48 ± 0.01	0.029 ± 0.007	
10.5	3.2×10^{-11}	0.056 ± 0.002	0.48 ± 0.01	0.12 ± 0.01	0.29 ± 0.03
10.0	1.0×10^{-10}	0.143 ± 0.006	0.48 ± 0.01	0.30 ± 0.01	

The reaction of triazinane **9** with HS^- was considerably slower than the reaction of the other triazinanes. Hence, the changes in the ^1H NMR spectra were smaller and random errors in the integration became significant. This is reflected in the large uncertainties in the regressions of k_1', which were up to 20 %. However, at pH 10.0, where the reaction is faster, the residual is smaller, only 4 %. As a result, the uncertainties in the determination of the rate constants were up to 24 % for k_2'. The uncertainty of k_3' was found to be 10 % from the linear regression.

7.3 2,4,6-Trimethyl-1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane

So far, only 1,3,5-triazinanes with various substituents on the nitrogen atoms in 1-, 3- and 5-position had been examined as H_2S-scavengers. An interesting next step would be to examine the effect of substituents on the ring carbon in 2-, 4- and 6-position on the reactivity and stability of the triazinane molecule. The simplest approach would be to make a triazinane with methyl groups in these positions, and attempts were made to synthesize 2,4,6-trimethyl-1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane (**10**). Triazinane **1** is made by mixing ethanolamine (**5**) and formaldehyde at room temperature. It was assumed that **10** could be formed in the same way by reacting ethanolamine (**5**) with acetaldehyde; hence the two reagents were mixed. A ^1H NMR spectrum of the reaction mixture is shown in Figure 7.7.

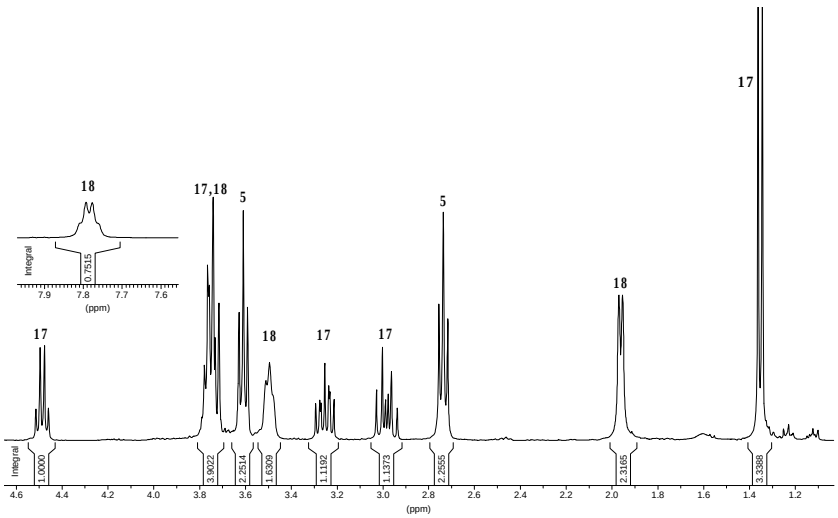


Figure 7.7 Reaction mixture, synthesis of** 10 **(300 MHz, $CDCl_3$).

The reaction mixture was also analysed by ^{13}C NMR, $^{1}H,^{1}H$, COSY and HET-COR spectroscopy. The NMR data are presented in Table 7.8.

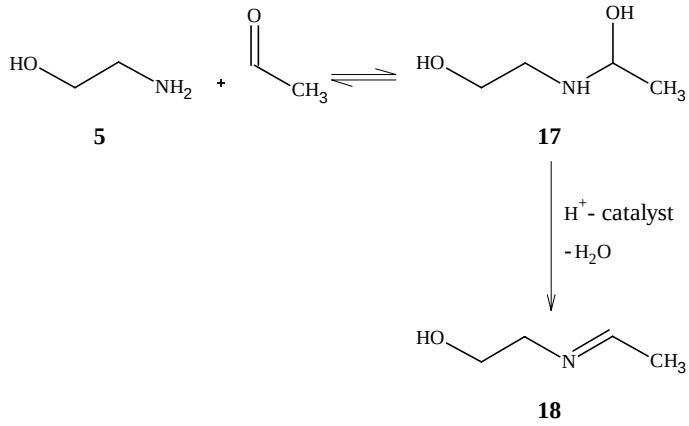
Table 7.8 Experimental NMR data for the reaction between** 5 **and acetaldehyde.

^{1}H NMR δ (ppm)	**Multi-plicity**	***J* (Hz)**	**^{13}C NMR δ (ppm)**	**^{1}H NMR coupling to δ (ppm)**	**Compound number**
1.35	d	5.7	20.9	4.49	**17**
1.96	d	5.1	23.8	7.78	**18**
2.74	t	5.4-5.7	45.3	3.61	**5**
2.99	m	-	47.8	3.23 3.75	**17**
3.23	m	-	47.8	2.99 3.75	**17**
3.49	t	5.1	64.3	3.75	**18**
3.61	t	5.7	65.8	2.74	**5**
3.75	m	-	67.4	2.99 3.23 3.49	**17+18**
4.49	q	5.4-5.7	91.3	1.35	**17**
7.78	q	5.1	169.8	1.96	**18**

The signals at δ 2.74 and 3.61 ppm are recognized as ethanolamine (**5**) by comparison with ^{13}C NMR data of the pure compound (Appendix B). The other signals belong to two new compounds, neither of which being acetaldehyde.

Compound **18** from the table has a methine group with very high shift values in both ^{1}H (δ 7.78 ppm) and ^{13}C NMR (δ 169.8 ppm). These shifts are in the region for sp^2-hybridized carbons and cannot originate from triazinane **10**.

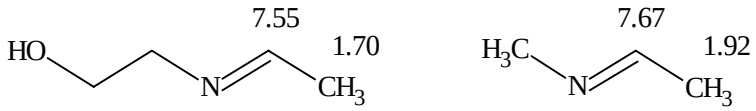
Imines are normally generated by reacting a ketone or an aldehyde with a primary amine.[4] This is shown in Scheme 7.3 for ethanolamine (**5**) and acetaldehyde.



Scheme 7.3 Formation of imine** 18 **from ethanolamine (**5**) and acetaldehyde.

The formation of 2-(ethylideneamino)ethanol (**18**) from **5** and acetaldehyde would be in accordance with the work of Carter *et al.*, where methylamine (**14**) and acetaldehyde were reacted in order to form the hexamethyl-substituted 1,3,5-triazinane.[21] The corresponding imine was a by-product. When ethylamine (**11**) was reacted with acetaldehyde, only the imine was formed.[21] Therefore, ethanolamine (**5**) and acetaldehyde would be expected to form the imine compound (**18**), rather than the wanted triazinane.

In conclusion, one of the compounds in the mixture was identified as 2-(ethylideneamino)ethanol (**18**), and its shift values have been assigned to that compound in Table 7.8. In the literature, ^{1}H NMR shifts for imine **18** and a similar compound, N-ethylidene-methanamine (**19**) were found.[20,21] The shifts are presented in Figure 7.8.



18 **19**

Figure 7.8 Literature ^{1}H NMR shifts for 18[20] and 19[21] (ppm).

In this work, the corresponding shifts for imine **18** were found to be δ 7.78 and 1.96 ppm. The reference[20] for imine **18** does not indicate which solvent was used, so the shifts cannot easily be compared. The ^{1}H NMR analysis of **19** was performed using the same solvent as the one used in this work ($CDCl_3$), and the shifts from the imine moiety are comparable. The literature values support the assignment of imine **18** to the NMR data in Table 7.8.

Imine **18** is assumed to be formed from acetaldehyde and ethanolamine (**5**) via 2-(1-hydroxyethylamino)ethanol (**17**) as indicated in Scheme 7.3. This reaction is acid-catalysed and at the relatively high pH levels that is found in this reaction mixture, it cannot be excluded that both **17** and **18** can be present simultaneously. The last step of the reaction in Scheme 7.3 is really an equilibrium reaction, but the addition of water to imine **18**, with the formation of **17**, is not very favourable, and this reaction is often neglected.

Compound **17** in Scheme 7.3 contains a chiral centre at the tertiary carbon atom. This chirality will affect the two prochiral methylene groups of the hydroxyethyl-substituent, making the methylene protons diastereotopic. They are magnetically and chemically non-equivalent, and will appear as a doublet of doublet of doublet in a ^{1}H NMR spectrum. This corresponds well with compound **17** in Table 7.8.

Compound **17** contains a methyl-group (the doublet at δ 1.35 ppm) bonded to a CH-group (the quartet at δ 4.49 ppm). In addition, the compound has a substituent in which the carbons bear two chemically non-equivalent protons. These protons are found at δ 2.99 and 3.23 ppm for the carbon closest to the nitrogen, and the splitting of the signals corresponds with a doublet of doublet of doublet, with the largest coupling constant being 12.0 Hz. This coupling constant represents the geminal coupling between the two protons at δ 2.99 and 3.23 ppm. Each of the protons have vicinal couplings to two other protons,

with coupling constants of 6.7 and 5.1-5.3 Hz for the proton at δ 3.23 ppm, and two times 7.7 Hz for the proton at δ 2.99 ppm. These constants represent the coupling between the two protons and the two magnetically non-equivalent protons on the carbon closest to the hydroxyl group. These protons, in turn, accidentally have identical chemical shifts and appear as a multiplet at δ 3.75 ppm, together with one of the triplets of imine **18**. This interference makes it difficult to establish the splitting pattern of the multiplet, but coupling constants of 12.0, 7.7, 6.7 and 5.2 Hz was found inside the multiplet. Hence, it was concluded that **17** was formed in the reaction between ethanolamine (**5**) and acetaldehyde.

The desired product, triazinane **10**, is not likely to show such a behaviour in ^{1}H NMR spectroscopy. Even though the substituents on the ring may have significantly increased the barrier of rotation for the methylene group closest to the ring nitrogen, the two protons of this group will most probably be chemically equivalent in the most stable rotamer, due to the symmetry of the molecule. Hence, the structure of triazinane **10** does not correspond with the signals of compounds **17** in Table 7.8. Nor does it correspond with the signals of imine **18**, which has a methine group with shift in the area of sp^2-hybridized carbons values in both ^{1}H (δ 7.78 ppm) and ^{13}C NMR (δ 169.8 ppm). Consequently, it was concluded that the wanted product, 2,4,6-trimethyl-1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane (**10**) could not be formed in this way.

7.4 Comparison of the Results

In the previous sections, the stability and reactivity of two new triazinanes, compounds **8** and **9**, have been examined, using the same procedures as for triazinane **1**.

7.4.1 Stability

Triazinanes **1**, **8** and **9** were analysed on the same day, by the NMR method described in Section 3.2. All the compounds followed the same rate expression, given in Equation 3-1. The rate constants k_1 and k_2 were determined for the three triazinanes, and triazinane half-lives were calculated from the rate

constants and Equation 3-6. The half-lives of the respective triazinanes are compared in Figure 7.9.

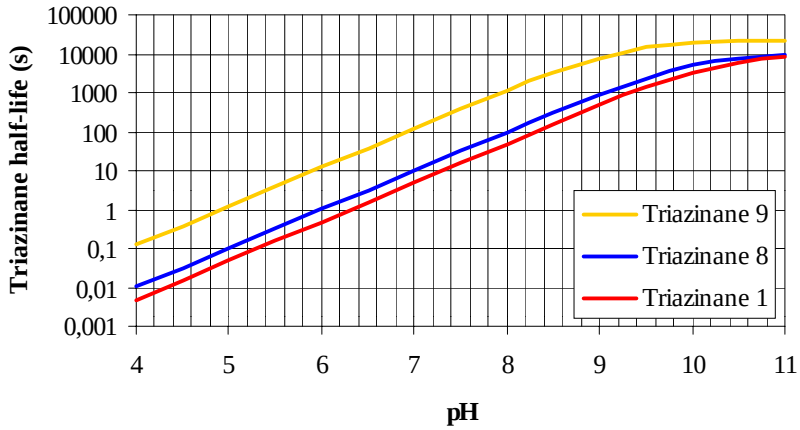


***Figure 7.9 Half-lives for triazinanes** 1,8 **and** 9.*

Figure 7.9 demonstrates that the methyl-substituted triazinane (**9**) is the most stable compound. At any given pH it will hydrolyse considerably slower than the triazinanes with larger substituents (**1** and **8**). It was also found that the ethyl-substituted triazinane (**8**) was more stable than the hydroxyethyl-substituted triazinane **1**. These results show that an increase in the chain length of the alkyl-substituent decreases the stability of the triazinane, and it becomes more susceptible to hydrolysis.

7.4.2 Reactivity with H_2S

The three triazinanes **1**, **8** and **9** were analysed by the method described in Section 6.3. The results are presented in Sections 6.3.1, 7.1.3 and 7.2.3, respectively. For all compounds, the rate constant k_3' in Equation 6-3 was determined. The rate constant k in the original rate expression (Equation 6-1) could not be used as a basis for the comparison of the rates of reaction, as the pK_a values for the triazinanes were not found in the literature. However, k depends solely on k_3' and K_a, and if it can be assumed that K_a is comparable for the three compounds, k_3' will give a good indication of which compound reacts faster with H_2S.

From literature, pK_a values of more simple amines were found.[3] To find out if the pK_a is expected to change considerably with alkyl chain length for a given

amine, pK_a values of simple substituted amines were compared (see Table 7.9).

Table 7.9 pK_a values of simple substituted amines.[3]

R	NH_2R	NHR_2	NR_3
Me	10.66	10.73	9.80
Et	10.65	10.84	10.75
Pr	10.54-10.63	11.05	
Bu	10.56-10.68		
EtOH	9.50		7.76

From Table 7.9 it was assumed that triazinane **1** will have a lower pK_a value (higher K_a) than triazinanes **8** and **9**. However, no conclusions can be made regarding the pK_a values of **8** and **9** relative to each other, although the data indicate that **8** will have a higher pK_a than **9**. Solving Equation 6-4 for k yields

$$k = k_3^{'} \cdot K_a \tag{7-1}$$

For triazinane **1**, k_3' was found to be 8.8×10^7 $M^{-2}s^{-1}$. Likewise, k_3' was found to be 5.5×10^7 $M^{-2}s^{-1}$ for triazinane **8** and 1.4×10^6 $M^{-2}s^{-1}$ for triazinane **9**. Hence, triazinane **1** has larger values than the two others both in terms of k_3' and K_a. Accordingly, it has a larger rate constant k and clearly reacts faster with HS^-.

The reactivities of **8** and **9** cannot be distinguished from these results, since **8** has a higher k_3', but may have a lower K_a than **9**. Therefore, it remains undetermined which of the two triazinanes react faster with HS^- at a given set of reaction conditions.

7.5 Conclusion

The rates of hydrolysis of 1,3,5-triethyl-1,3,5-triazinane (**8**) and 1,3,5-trimethyl-1,3,5-triazinane (**9**) were examined by the same method as that used for triazinane **1**, and the rate expression and rate constants were found to be:

$$-\frac{d[T]}{dt} = k_1[T] + k_2[T][H^+]$$

where

$k_1 = 7\times10^{-5}\ s^{-1}$ $k_2 = 6.9\times10^{5}\ M^{-1}s^{-1}$

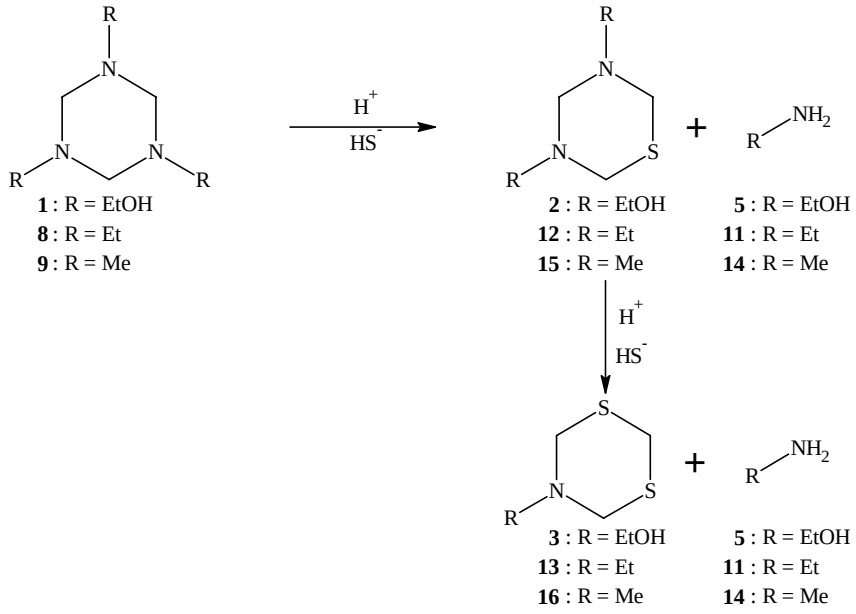
for triazinane **8**, and

$k_1 = 3\times10^{-5}\ s^{-1}$ $k_2 = 5.8\times10^{4}\ M^{-1}s^{-1}$

for triazinane **9**.

The estimates of k_1 for the two compounds have very high uncertainties, and the accuracy of the results is good only at pH levels where the k_1 term can be neglected, which is below 9 for triazinane **8** and below 8 for triazinane **9**. The corresponding values for triazinane **1** are $k_1 = 7\times10^{-5}\ s^{-1}$ and $k_2 = 1.41\times10^{6}\ M^{-1}s^{-1}$. It was concluded that triazinane **1** hydrolyses faster than triazinane **8**, which in turn hydrolyses faster than triazinane **9**.

The reaction between H_2S and each of the triazinanes **8** and **9** were studied. For both, the reaction was found to proceed in the same way as the reaction involving triazinane **1**. The results are summarized in Scheme 7.4.



Scheme 7.4 The reaction between 1,3,5-triazinanes and H_2S.

The reactivity of the two triazinanes with HS^- were studied, and the rate expression for both reactions was

$$-\frac{d[T]}{dt} = k[TH^+][HS^-]$$

in which $k = K_a \cdot k_3'$, and k_3' was found to be

$$k_3' = 5.5\times10^7\ M^{-2}s^{-1}$$

for triazinane **8**, and

$$k_3' = 1.4\times10^6\ M^{-2}s^{-1}$$

for triazinane **9**.

For triazinane **1**, the corresponding value is $k_3' = 8.8\times10^7\ M^{-2}s^{-1}$. It was concluded that **1** also has a larger K_a and a larger rate constant k than the two other compounds, making it the most reactive of the triazinanes in H_2S removal.

From these experiments, it was concluded that triazinane **1** is the most reactive of the compounds, but it is also easier hydrolysed. Triazinanes **8** and **9** were not better suited as H_2S-scavengers under the currently studied conditions, but they may compete with triazinane **1** in situations where stability becomes more important than the reactivity of the scavenger.

Attempts to synthesize another 1,3,5-triazinane, 1,3,5-tris(2-hydroxyethyl)-2,4,6-trimethyl-1,3,5-triazinane (**10**), from acetaldehyde and ethanolamine (**5**) were not successful.

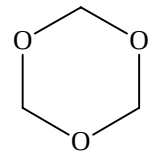
8 Stability and Reactivity of Trioxanes, Tetroxanes and an Oxolane

So far, only triazinanes have been considered as liquid H_2S scavengers. However, the methods developed in this work for the testing of scavenger stability and reactivity are applicable to most organic compounds.

Another class of compounds that is expected to be reactive towards H_2S is formaldehyde and derivatives thereof. Formaldehyde derivatives and similar compounds that are easier to handle may possess the same reactivity, and analyses of some of them are presented in this chapter.

8.1 1,3,5-Trioxane

1,3,5-trioxane (**20**) is a trimer of formaldehyde, and it is frequently used as a formaldehyde source in organic synthesis. Its structure is shown in Figure 8.1.



20

Figure 8.1 Structure of 1,3,5-trioxane (*20*).

Commercially available 1,3,5-trioxane was analysed by ^1H NMR spectroscopy using both D_2O and $CDCl_3$ as solvents. From the spectra, it seems that only trioxane **20** is present, and the compound has higher ^1H and ^{13}C shift values than formaldehyde in both solvents.

Trioxane **20** was mixed with Na_2S in an aqueous buffer at pH 10.0. No change was observed after five hours, neither in the ^1H NMR spectrum nor in the reaction mixture. It was concluded that **20** reacts extremely slow, if at all, with Na_2S at pH 10.0.

In a parallel experiment, formaldehyde and Na_2S were mixed in an aqueous buffer of pH 10.0. After five hours, only the water signal was observed in the ^1H NMR spectrum, but it was assumed that the formaldehyde dihydrate signal was present inside the water signal. No new products had been formed. However, the reaction mixture was left for three days, after which a white solid had

precipitated from the solution. In the trioxane/Na_2S mixture, no solids were observed after three days. The white solid is assumed to be a polymer of the type $(-CH_2-S-)_n$, but it was insoluble in six tested solvents, ranging from water to hexane in polarity, and could not be analysed.

It was necessary to see if any reaction occurred between 1,3,5-trioxane (**20**) and HS^- at lower pH levels. The equimolar reaction between **20** and NaHS was again performed, but this time the pH was kept constant at 7.0. After six hours, no reaction product was found in the ^1H or ^{13}C NMR spectra, but some white solid had precipitated from the solution.

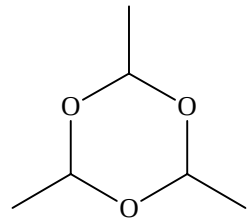
The previous experiments raised the question whether trioxane **20** is present as the trimer or as formaldehyde dihydrate in the aqueous solutions used. The stability of **20** was analysed at pH 5.5, 2.5 and 1.5. The three samples had identical concentrations of **20** and the IS (acetonitrile), and a ^1H NMR spectrum of the pH 5.5 solution was immediately recorded. The relative amounts of **20** and the IS in this spectrum were used as a basis of comparison with the spectra of the three solutions later recorded. After 25 hours, both ^1H and ^{13}C NMR spectra of the solutions were recorded. Trioxane **20** and the IS were still the only compounds in the mixture, and the relative intensities of the signals from **20** and the IS had not changed. Hence, **20** was considered to be stable even at very low pH levels.

Finally, gaseous H_2S was bubbled through an aqueous solution containing **20** and acetonitrile as an internal standard for 25 minutes, giving pH of 5 in the solution. Two hours later a ^1H NMR spectrum indicated that the relative amounts of **20** and the IS were unchanged, and no products had been formed. No precipitation of any solids was observed.

From these experiments it was concluded that 1,3,5-trioxane (**20**) reacted very slowly, if at all, with HS^-. However, the results do not exclude the possibility that the trioxane coordinates to the sulfide and hence increases the uptake of H_2S in a solution. This effect would not be observable with the methods used in the previous sections, but the experiments nevertheless indicate that 1,3,5-trioxane (**20**) cannot compete with 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane (**1**) as an H_2S scavenger.

8.2 2,4,6-Trimethyl-1,3,5-trioxane

The studies of 1,3,5-trioxane (**20**) as an H_2S scavenger was complicated by the fact that the ^1H NMR signals of the monomer of **20**, and a possible hydrolysis product formaldehyde dihydrate interfered with the large water signal in the spectra. The substituted trioxane 2,4,6-trimethyl-1,3,5-trioxane (**21**) is a trimer of acetaldehyde, which was expected to be easier to observe in ^1H NMR, since the methyl signal does not interfere with any other signals in the spectrum. The structure of **21** is shown in Figure 8.2.



21

Figure 8.2 Structure of 2,4,6-trimethyl-1,3,5-trioxane (21).

Initially, commercially available **21** and acetaldehyde were analysed by ^1H NMR spectroscopy (see Appendix A). The spectra of the pure acetaldehyde contained two sets of signals, showing that both the aldehyde and the dihydrated form appear simultaneously.

2,4,6-trimethyl-1,3,5-trioxane (**21**) was reacted with one equivalent of NaHS at pH 10.0. The progress was followed by ^1H NMR spectroscopy, but even after three days, no change was observed in the spectrum. The pH was lowered to 7.0, and the mixture was left for another day, after which a new spectrum showed that no reaction had occurred. Trioxane **21** was still intact, and no trace of any of the acetaldehyde forms was observed.

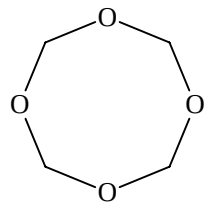
A final experiment was performed, in which gaseous H_2S was bubbled through an aqueous solution of **21** and acetonitrile as an internal standard for 20 minutes. No significant change in the relative amounts of **21** and the IS was found in the ^1H NMR spectrum, and no new products was observed. Furthermore, no solid was formed.

The results of these experiments, together with the results from the previous section, show that simple trioxanes like **20** and **21** are not efficient in H_2S scavenging. They are stable compounds compared to the triazinanes, but they

cannot compete with the tested triazinanes as H_2S scavengers, due to their lack of reaction with H_2S.

8.3 1,3,5,7-Tetroxane

As the studies of the trioxanes in the previous sections indicated that these compounds were not reactive towards the sulfide nucleophile, new structures had to be considered. An increase in the ring size is expected to increase the reactivity of the compound, and for this reason, attempts were made to synthesize 1,3,5,7-tetroxane (**22**).



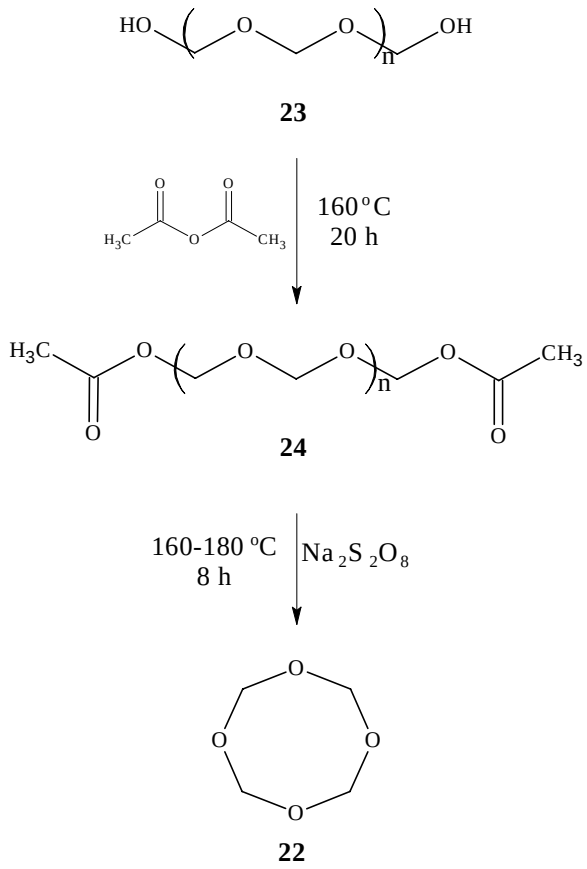
22

Figure 8.3 The structure of 1,3,5,7-tetroxane (*22*).

Compound **22** is a well-known compound, and its synthesis have been reported by Miyake *et al*.[23] In this procedure, paraformaldehyde (**23**) was used as starting material, and the terminal hydroxyl groups of the chain were stabilized by converting them to acetate moieties. The paraformaldehyde diacetate (**24**) was then thermally cleaved to yield 1,3,5,7-tetroxane (**22**).

The challenge in this synthesis is to minimize the formation of 1,3,5-trioxane (**20**) and maximize the yield of the desired tetroxane (**22**). According to the reference, this can be achieved in two ways. Firstly, a catalyst can be used that cleaves the paraformaldehyde diacetate (**24**) at the right locations. Tetroxane **22** is formed after the following ring closure. Potassium persulfate was found to be the best catalyst.[23] Secondly, tetroxane **22**, which is formed before trioxane **20**, can be continuously removed from the reaction mixture by extraction, as trioxane **20** is the thermodynamically favoured product and will be the dominant component if the reaction mixture is given time to stabilize.[23]

The method using the catalyst was preferred, and this method is summarized in Scheme 8.1.



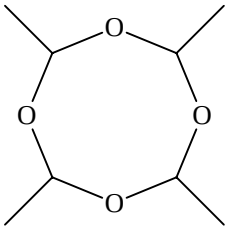
Scheme 8.1 Formation of tetroxane** 22 **from paraformaldehyde (**23**).

Paraformaldehyde (**23**) and acetic anhydride were mixed and heated to 160 °C. Acetic anhydride has a boiling point of 140 °C and was present in gaseous form inside the autoclave. After 20 hours, some white solid was left in the bottom of the autoclave, while the rest had sublimed and was present in the top. The remaining acetic anhydride was washed away with diethyl ether and ethyl acetate. It proved to be difficult to establish whether the white solid inside the container was the wanted diacetate (**24**) or not. The solid melted around 180 °C. The melting point of paraformaldehyde is 164 °C.[3]

The catalyst (solid $Na_2S_2O_8$) was added to the white solid, and the mixture was heated to 160 °C for 2.5 hours. The wanted product, 1,3,5,7-tetroxane (**22**), has a melting point of 105-110 °C and were to be collected by a cold trap of -78 °C if formed. However, no product was observed in the cold traps after 2.5 hours. The white solid was unchanged, and the experiment was stopped.

In a second attempt, more reagents were used in order to saturate the air i the autoclave with the acetic anhydride vapour. Again, the sublimed matter was isolated and washed with diethyl ether and ethyl acetate. The solid was mixed with twice the amount of catalyst as in the previous attempt. The mixture was heated in a standard sublimator in order to minimise the distance between the solid and the cooler. No solid was observed on the cold finger. In a third attempt, $K_2S_2O_8$ replaced $Na_2S_2O_8$ as the catalyst. A standard sublimator was used. Again, none of the desired tetroxane (**22**) was formed.

Even though it proved to be difficult to synthesize the wanted 1,3,5,7-tetroxane (**22**), it would still be interesting to see if this class of compounds possess an increased reactivity because of their ring tension. The methyl-substituted tetroxane 2,4,6,8-tetramethyl-1,3,5,7-tetroxane (**25**) is commercially available and could be tested. Its structure is shown in Figure 8.4.



25

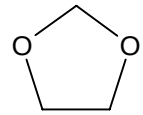
Figure 8.4 Structure of 2,4,6,8-tetramethyl-1,3,5,7-tetroxane (25).

However, **25** is insoluble in water, ethanol, diethyl ether, chloroform, THF, DMSO, 1,4-dioxane, pentane and acetone and could not be analysed.

From these experiments it could not be excluded that tetroxane compounds are active towards H_2S and other nucleophiles because of their ring tension, but the difficulties in synthesising them, and their low solubility, make them economically and environmentally unfavourable as H_2S-scavengers.

8.4 1,3-Dioxolane

1,3-dioxolane (**26**) is a condensation product between 1,2-ethanediol and formaldehyde. It is commercially available, and its structure is shown in Figure 8.5.



26

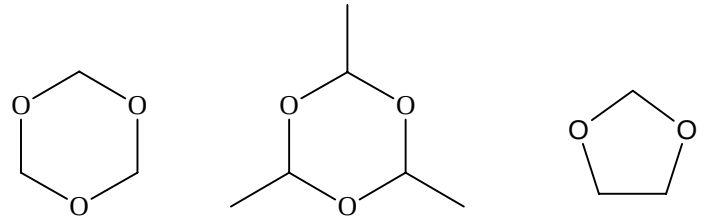
Figure 8.5 Structure of 1,3-dioxolane (*26*).

Initial ^{1}H NMR analyses of the compound were performed, and they showed that the compound was pure and only present in its cyclic form. The ^{1}H NMR data of the pure compound are presented in Appendix A.

In order to see if **26** is reactive towards H_2S, two experiments were performed, in which H_2S-gas was bubbled through a solution of **26** in water. Acetonitrile was used as an internal standard (IS). In the first experiment, the supply of H_2S was stopped after 5 minutes. The solution had a pH of 4. After additional 70 minutes of reaction time, a ^{1}H NMR spectrum was recorded. No new products was observed in the spectrum. Moreover, the relative amounts of **26** and the IS showed that all the reagent was intact. A ^{13}C NMR spectrum was recorded, but no signals was found, besides the signals from **26** and acetonitrile. The next experiment was similarly performed, but this time the addition of H_2S was stopped after 35 minutes. After a reaction time of 30 minutes, a ^{1}H NMR spectrum of the reaction mixture showed only the signals from **26** and the IS, and their relative amounts were the same as in the initial ^{1}H NMR spectrum. Again, this was confirmed by a ^{13}C NMR spectrum.

8.5 Conclusion

Several cyclic formaldehyde derivatives were analysed in order to establish whether they showed any reactivity towards H_2S. The structure of the compounds tested are shown in Figure 8.6.

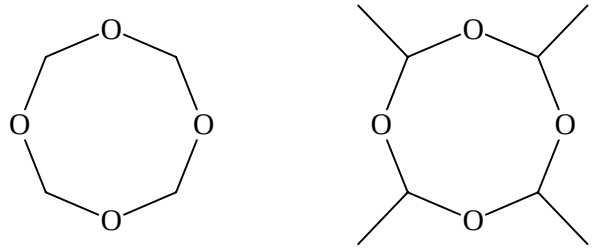


20 **21** **26**

Figure 8.6 Structures of tested formaldehyde derivatives.

From NMR spectroscopy, none of the compounds in Figure 8.6 formed any new products upon reaction with H_2S or HS^-. Although this indicates that the compounds are unreactive towards H_2S, it cannot be ruled out that they assist the H_2S removal by forming complexes. However, as these reactions will not cause any change in the NMR spectra, their potential as H_2S scavengers cannot be studied by the methods applied in this work.

Another class of compounds, 1,3,5,7-tetroxanes, were assumed to be reactive towards H_2S because of their ring tension. Tetroxanes are 8-membered heterocyclic compounds, and the structures of the two tested compounds are presented in Figure 8.7.



22 **25**

Figure 8.7 Structures of tetroxanes** 22 **and** 25**.

The synthesis of 1,3,5,7-tetroxane (**22**) was not successful, and commercially available 2,4,6,8-tetramethyl-1,3,5,7-tetroxane (**25**) was unsuitable for the analyses performed here because of its low solubility in most solvents.

From these experiments, it cannot be excluded that tetroxanes **22** and **25** are reactive towards H_2S, but it is assumed that they will be economically unfavourable as H_2S scavengers. This is due to the complexity of the synthesis of **22**, and the poor solubility of **25**.

9 Experimental

9.1 General

9.1.1 Chemicals

All chemicals and solvents were of synthetic grade and were used without further purification. All water solutions were made with distilled water. Unless otherwise indicated, all buffered solutions were made from a 0.50 M solution of Na_2HPO_4, and all pH adjustments were performed with solid K_2CO_3, concentrated HCl or solid NaH_2PO_4. Solid Na_2S and NaHS were used as sources of HS^-, and their purities were 60-62 % and 68-72 %, respectively, the rest being crystal water.

9.1.2 Instrumentation

NMR Spectroscopy

^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance DPX300 or DPX400 instruments. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS, in $CDCl_3$) or sodium 3-(trimethylsilyl)propionate-2,2,3,3-d_4 (in D_2O and CD_3OD). In some experiments, a D_2O-buffer was used as solvent. The term "D_2O-buffer" will refer to a 0.50 M solution of Na_2HPO_4 in D_2O, in which the pH had been adjusted to 10.0 with solid K_2CO_3.

All NMR spectra were recorded at room temperature with D_2O as solvent unless otherwise indicated.

Mass Spectrometry

The EIMS analysis and HRMS were performed on a Finnigan MAT 95 XL instrument. The temperature was 20°C throughout the analysis.

IR Spectroscopy

Infrared spectra were recorded on a Nicolet 20SXC FT-IR Spectrometer.

Gas Chromatography

GC analyses were performed on two different GCs:

1. Chrompack 9000, Model 910/911 with split injection, flame ionisation detector, and a Shimadzu C-R5A integrator. The column used was CP-Sil5CB (25 m, ID 0.33 mm, D_f 0.45 μm). The temperature program used

linear gradients between the temperatures 80°C (0 min) - 180°C (12.5 min) - 250°C (16 min)- 180 °C (36 min).

2. Carlos Erba Instruments GC 6000 Vega Series 2 with on-column injection. The detectorand integrator were identical with the ones in GC system 1. The column was RTX-5 Amine (30 m, ID 0.25 mm, D_f 0.5 µm). The temperature program used was 80°C (0 min)- 80 °C (3 min) - 250°C (11.5 min) - 250 °C (14.5 min).

All GC chromatograms were obtained by dissolving the pure component to be analysed in dichloromethane (GC system 1) or methanol (GC system 2).

Thin Layer and Column Chromatography

TLC analyses were performed on Merck TLC aluminium sheets with Silica gel 60 F_{254}. The plates were developed with phosphomolybdic acid.

Silica 60 AC.C 40-63 µm was used as stationary phase in column chromatography.

pH Measurements

Unless otherwise indicated, measurements of pH were performed with an Orion Ross Sure-Flow Combination electrode, model 8172, which can be used with sulfide-containing solutions. The electrode was connected to a constant-pH apparatus. This apparatus can keep a solution at a certain pH level by automatic titration. When pH rises above this level, an acidic solution is added with a Masterflex Easy-load pump (model 5718-00). Unless otherwise indicated, a 5 % aqueous solution of HCl was used to keep the pH constant.

Sulfide Detection

Detection of sulfide was done with an Orion Sure-Flow Combination Silver/ Sulfide Electrode, model 9616, connected to a Fluke 89IV True RMS Multimeter.

Elemental Analysis

Elemental Analyses were performed by the Laboratory of Organic Elemental Analysis, Prague Institute of Chemical Technology, Czech Republic.

Melting Points

All melting points are uncorrected and were measured on a Büchi oil bath melting point apparatus.

9.2 The Synthesis of Triazinane 1

Ethanolamine (**5**, 18.0 g, 0.295 mol) and ethanol (2.40 g, 0.0521 mol) were mixed and stirred for 15 minutes at room temperature. Aqueous formaldehyde (37 wt%, 22.0 g, 0.291 mol) was added dropwise. The temperature in the reaction mixture was kept below room temperature by placing the reaction flask in an water bath, cooled with ice. The reaction mixture was then left at room temperature for 1-2 hours. As much water as possible was evaporated from the product under reduced pressure, and the structure of the liquid product was analysed by ^{1}H NMR spectroscopy. In this way, **1** was synthesized in 90 % yield. The product was a viscous, yellow oil with a typical purity of 70 % from ^{1}H NMR, the rest being unreacted ethanolamine (**5**) and water. NMR data for commercial ethanolamine (**5**) and formaldehyde are given in Appendix A and Section 9.3.1. The synthesized **1** was used as a reagent in several experiments, and it is important to bear in mind that the isolated **1** contained traces of both water, ethanolamine (**5**) and formaldehyde, the latter two being formed upon storage.

*Triazinane **1**:*

^{1}H NMR (300 MHz, D_2O): δ 2.69 (t, *J* = 5.8 Hz, N-C$\underline{H}_2$-CH_2-OH), 3.49 (br. s, N-C$\underline{H}_2$-N), 3.70 (t, *J* = 5.8 Hz, N-CH_2-C$\underline{H}_2$-OH).

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.65 (t, *J* = 4.9-5.3 Hz, N-C$\underline{H}_2$-CH_2-OH), 3.50 (br. s, N-C$\underline{H}_2$-N), 3.68 (t, *J* = 4.9-5.3 Hz, N-CH_2-C$\underline{H}_2$-OH).

^{13}C NMR (75 MHz, D_2O): δ 56.5 (N-$\underline{C}H_2$-CH_2-OH), 60.0 (N-CH_2-$\underline{C}H_2$-OH), 75.7 (N-$\underline{C}H_2$-N).

9.3 The Hydrolysis of Triazinane 1

9.3.1 The Structures of the Products

1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane (**1**, 70 %, 0.26 g, 0.83 mmol) was dissolved in distilled water (10.0 ml). The solution was acidified to pH 1.5 with concentrated H_2SO_4.

Ethanolamine (**5**, 0.26 g, 4.3 mmol) was dissolved in water (10.0 ml). The solution was acidified to pH 1.5 with concentrated H_2SO_4.

NMR samples were taken from both solutions and diluted in D_2O. Ethanolamine (**5**) and aqueous formaldehyde (37 wt%) were also analysed as references.

*Hydrolysed **1**, pH 1.5:*

^{1}H NMR (400 MHz, D_2O): δ 3.13 (t, *J* = 4.9-5.1 Hz, H_2N-C$\underline{H}_2$-CH_2-OH), 3.81 (t, *J* = 5.1-5.4 Hz, H_2N-CH_2-C$\underline{H}_2$-OH).

^{13}C NMR (100 MHz, D_2O): δ 44.2 (H_2N-$\underline{C}H_2$-CH_2-OH), 60.6 (H_2N-CH_2-$\underline{C}H_2$-OH), 84.7 (HO-$\underline{C}H_2$-OH).

*Ethanolamine (**5**), pH 1.5:*

^{1}H NMR (400 MHz, D_2O): δ 3.13 (t, *J* = 4.9-5.2 Hz, H_2N-C$\underline{H}_2$-CH_2-OH), 3.81 (t, *J* = 5.2-5.3 Hz, H_2N-CH_2-C$\underline{H}_2$-OH).

*Ethanolamine (**5**):*

^{1}H NMR (300 MHz, D_2O): δ 2.73 (t, *J* = 5.6 Hz, H_2N-C$\underline{H}_2$-CH_2-OH), 3.61 (t, *J* = 5.6 Hz, H_2N-CH_2-C$\underline{H}_2$-OH).

Aqueous Formaldehyde:

^{1}H NMR (400 MHz, D_2O): δ 4.83 (s, HO-C$\underline{H}_2$-OH).

^{13}C NMR (100 MHz, D_2O): δ 84.6 (s, HO-$\underline{C}H_2$-OH).

9.3.2 The Rate of Hydrolysis

The rate of hydrolysis of **1** were determined at various pHs and two temperatures, 22 and 60 °C, by the use of ^{1}H NMR spectroscopy. At 22 °C, the reaction was monitored at pH 10.0, 9.0 and 8.0. At 60 °C, the reaction was monitored at pH 10.9 and 9.5 only.

For kinetic measurements, was 0.1 vol%. **1** (200 µl of a 5 % solution) was added to a buffer solution (10.0 ml) of the desired pH to yield a 0.1 vol% solution of **1**. The time was set to zero when the solution and the buffer was mixed.

At 22 °C, the hydrolysis was performed in an NMR tube in the spectrometer and spectra were recorded with fixed intervals (3 minutes at pH 10.0, 2 minutes at pH 9. 0, and 1 minute at pH 8.0).

At 60 °C, the hydrolysis was performed in a large-scale reaction mixture, from which samples of 0.4 ml were taken, quenched by addition of a potassium carbonate solution, and stored in an ice bath.

The concentrations of **1** in both cases were determined by ^{1}H NMR spectroscopy with acetonitrile as an internal standard (IS). For **1** the triplet at 2.70 ppm in the NMR spectra was used to determine its concentration.

Buffer Solutions (22 °C):

pH 10.0: 0.50 M Na_2HPO_4 solution in D_2O adjusted to pH 10.0 with solid K_2CO_3.

pH 9.0: 0.50 M Na_2HPO_4 solution in D_2O acidified to pH 9.0 with solid NaH_2PO_4.

pH 8.0: 0.50 M Na_2HPO_4 solution in D_2O acidified to pH 8.0 with solid NaH_2PO_4.

Buffer Solutions (60 °C):

pH 10.9: 0.50 M Na_2HPO_4 solution in D_2O adjusted to pH 10.9 with solid K_2CO_3.

pH 9.5: 0.50 M K_2CO_3 solution in D_2O acidified to pH 9.5 with solid KH_2PO_4.

Solution for Quenching of Hydrolysis (60 °C):
2 M K_2CO_3 in D_2O acidified to pH 11.3 with solid KH_2PO_4.

Calculations, plotting and linear regressions were done in Microsoft Excel 97.

9.4 The Equimolar Reaction between Triazinane 1 and HS^-

9.4.1 NMR Analyses

*Triazinane **1** and Na_2S, Reaction Mixture*

Na_2S (60 %, 58 mg, 0.45 mmol) was dissolved in a D_2O-buffer of pH 10.0 (10.0 ml). The pH in the solution rose to 10.4, and it was lowered to 10.0 by addition of concentrated HCl. Triazinane **1** (70 %, 0.10 g, 0.32 mmol) was added, bringing the pH up to 10.2. As the reaction proceeded, pH increased and was kept between 10.0 and 10.5 by dropwise addition of concentrated

HCl. After 45 minutes, several NMR analyses were performed. The reaction was reproduced for the recording of the 1D NOE spectra.

^{1}H NMR (300 MHz, D_2O-buffer, pH 10): δ 2.69 (t, *J* = 5.7-6.0 Hz), 2.91 (t, *J* = 5.3-5.7 Hz), 3.04 (t, *J* = 5.7 Hz), 3.16 (t, *J* = 5.7 Hz), 3.61 (t, *J* = 5.7 Hz), 3.66 (t, *J* = 5.7-6.0 Hz), 3.70 (t), δ 3.71 (t, *J* = 5.3-5.7 Hz), 3.92 (s), 4.26 (s).

^{1}H,^{1}H COSY (300 MHz, D_2O-buffer, pH 10): δ 2.69 with 3.70, 2.91 with 3.71, 3.04 with 3.66, 3.16 with 3.61.

1D NOE (400 MHz, D_2O-buffer, pH 10): Irradiated: δ 3.04; affected: δ 3.66 (+ 6.3 %), 3.92 (+ 5.8 %), 4.26 (+ 1.6 %). Irradiated: δ 3.92; affected: δ 3.04 (+ 3.2 %). Irradiated: δ 4.26; affected: 3.04 (+ 1.5 %), 3.66 (+ 2.8 %), 3.92 (+ 2.0 %).

^{13}C NMR (75 MHz, D_2O-buffer, pH 10): δ 44.7, 46.0, 56.5, 56.7, 57.5, 60.0, 61.5, 63.7, 64.1, 75.7, 76.4.

^{1}H,^{13}C CORR (75 MHz, D_2O-buffer, pH 10): δ 44.7 (^{13}C) with 2.91 (^{1}H), 56.5 (^{13}C) with 2.69 (^{1}H), 56.7 (^{13}C) with 3.04 (^{1}H), 57.5 (^{13}C) with 4.26 (^{1}H), 61.5 (^{13}C) with 3.66 (^{1}H), 63.7 (^{13}C) with 3.71 (^{1}H), 64.1 (^{13}C) with 3.61 (^{1}H), 76.4 (^{13}C) with 3.92 (^{1}H).

*Investigation of Possible Products: 2-Mercaptoethanol (**6**)*

^{1}H NMR (300 MHz, D_2O): δ 2.69 (t, *J* = 6.1-6.3 Hz, HS-C$\underline{H}_2$-CH_2-OH), 3.71 (t, *J* = 6.1-6.2 Hz, HS-CH_2-C$\underline{H}_2$-OH).

^{1}H NMR (300 MHz, D_2O-buffer, pH 10): δ 2.66 (t, *J* = 6.8 Hz, HS-C$\underline{H}_2$-CH_2-OH), 3.65 (t, *J* = 6.8 Hz, HS-CH_2-C$\underline{H}_2$-OH).

^{13}C NMR (75 MHz, D_2O-buffer, pH 10): δ 28.8 (HS-$\underline{C}H_2$-CH_2-OH), 66.4 (HS-CH_2-$\underline{C}H_2$-OH).

*Investigation of Possible Products: 2,2'-[Methylenebis(imino)]diethanol (**7**)*

The first attempted synthesis of **7** was performed by reacting 2 equivalents of ethanolamine (**5**) with formaldehyde in the following way: Ethanolamine (**5**, 18 g, 0.29 mol) and ethanol (2.4 g, 0.052 mol) was mixed and stirred for 15 minutes at room temperature. Formaldehyde (37 wt%, 11.0 g, 0.145 mol) added dropwise over a period of 40 minutes. The temperature was kept between 25 °C and 40 °C by having the reaction flask placed on an water bath

cooled with ice. The reaction time was 2 hours. In the second run, the amount of ethanolamine (**5**) was doubled.

^{1}H NMR (300 MHz, D_2O-buffer, pH 10): δ 2.69 (t, *J* = 5.7-6.0 Hz, **1**), 2.91 (t, *J* = 5.3-5.7 Hz, **5**), 3.71 (t, *J* = 5.3-5.7 Hz, **5**+**1**). Traces: 3.16 (t, *J* = 5.7 Hz), 3.61 (t, *J* = 5.7 Hz).

^{13}C NMR (75 MHz, D_2O-buffer, pH 10): δ 44.7, 46.0, 56.5, 61.5, 63.8, 64.1, 75.7.

9.4.2 Separation and Isolation of the Products

Liquid/Liquid Extraction

Triazinane **1** (70 %, 4.0 g, 0.013 mol) was dissolved in water (80.0 ml). Na_2S (60 %, 2.3 g, 0.018 mol) was added. The pH was lowered to 10.0 with concentrated HCl. A ^{1}H NMR spectrum was recorded after 45 minutes.

^{1}H NMR (300 MHz, D_2O-buffer, pH 10): δ 2.69 (t, *J* = 5.7-6.0 Hz), 2.91 (t, *J* = 5.3-5.7 Hz), 3.04 (t, *J* = 5.7 Hz), 3.16 (t, *J* = 5.7 Hz), 3.61 (t, *J* = 5.7 Hz), 3.66 (t, *J* = 5.7-6.0 Hz), 3.70 (t), 3.71 (t, *J* = 5.3-5.7 Hz), 3.92 (s), 4.26 (s).

The reaction mixture was extracted with 6×20 ml (fraction 1), 3×20 ml (fraction 2), and 3×20 ml (fraction 3) dichloromethane. ^{1}H NMR spectra of the fractions showed that fraction 1 contained 76 % of thiadiazinane **2** and 24 % of the compound later identified as dithiazinane **3**. In fractions 2 and 3, only **2** was found, along with traces of ethanolamine (**5**). Dichloromethane was evaporated off fraction 1, and the resulting yellow oil was dissolved in water (25.0 ml) and extracted five times with 2×20 ml dichloromethane. The fractions were analysed by ^{1}H NMR, and all the extracts that contained more than 90 % of **2** were combined. The purity of the isolated **2** after evaporation of the solvent was 90 % by ^{1}H NMR, the main impurities being **3** and dichloromethane.

Thin Layer and Column Chromatography

Triazinane **1** (70 %, 1.0 g, 3.2 mmol) was dissolved in methanol (10.0 ml) and Na_2S (60 %, 0.57 g, 4.4 mmol) was added. ^{1}H NMR analysis performed in D_2O-buffer showed that **1**, **2**, and **5** were the main components of the solution. Traces of the unknown compound D (Section 4.1.5) were also found.

The reaction mixture was applied onto five TLC-plates, using five different mobile phases: methanol, methanol/ethyl acetate (1:4), ethyl acetate, ace-

tonitrile and hexane. In methanol and methanol/ethyl acetate, all the components moved from the baseline, but they were inseparable. In hexane, none of the components moved from the baseline. In ethyl acetate and acetonitrile, one component seemed to be separated from the rest (ΔR_f = 0.35 and 0.56, respectively).

For the column chromatography experiment, the sample was prepared by adding silica to the reaction mixture (10.0 ml), and removing the solvent by evaporation. The column was packed with silica and ethyl acetate. The column was eluated with ethyl acetate (400 ml), followed by ethyl acetate/methanol (1:1, 200 ml) and pure methanol (200 ml). The fractions that contained the separated spot were combined, and the solvent was evaporated off. NMR analysis were made of the product, which was identified as dithiazinane **3**.

^{1}H NMR (400 MHz, D_2O): δ 3.19 (t, *J* = 5.5-6.0 Hz), 3.71 (t, *J* = 5.5 Hz), 4.16 (s), 4.49 (s).

^{13}C NMR (100 MHz, D_2O): δ 35.1, 53.0, 60.0, 61.0.

9.4.3 Analyses of Thiadiazinane 2

Thiadiazinane **2** with a purity of 90 % was synthesized and isolated as described in Section 9.4.2.

Mass Analysis
Elemental analysis was performed on the isolated **2**.

Anal. Calcd. for $C_7H_{16}N_2O_2S$: C, 43.7; H, 8.4; N, 14.6; S, 16.7. Found: C, 42.4; H, 8.1; N, 14.0; S, 16.6.

Low Temperature ^{1}H NMR spectra
Thiadiazinane **2** was analysed by ^{1}H NMR spectroscopy at room temperature, -15 °C, -40 °C, -53 °C, -66 °C, and -79 °C. The ^{1}H NMR data for room temperature and -79 °C are given below.

^{1}H NMR (400 MHz, D_2O, 23 °C): δ 2.98 (t, *J* = 5.5-6.0 Hz), 3.53 (t, *J* = 5.7-5.8 Hz), 3.92 (s), 4.25 (s).

^{1}H NMR (400 MHz, D_2O, -79 °C): δ 2.89 (m), 3.33 (m), 3.56 (m), 3.79 (d, *J* = 13.7 Hz), 4.08 (d, *J* = 12.7 Hz), 4.33 (d, *J* = 13.8 Hz), 4.71 (d, *J* = 12.8 Hz).

IR Spectroscopy

IR (neat): ν/cm^{-1} 3378 (s), 2913 (s), 1429 (s), 1285 (m), 1176 (w), 1048 (m), 938 (w), 880 (w), 691 (w), 668 (w).

9.5 The Reaction between Triazinane 1 and Excess HS^-

9.5.1 Thiadiazine 2 and NaHS

Thiadiazinane **2** (90 %, 0.010 g, 0.047 mmol), isolated as described in Section 9.4.2 was dissolved in a buffered water solution of pH 10.0 (10.0 ml). NaHS (68 %, 0.0042 g, 0.051 mmol) was added and the pH was kept constant while the reaction proceeded. ^{1}H NMR spectra were recorded after 21 hours and after two days. The ^{13}C NMR spectrum was recorded after 2 days.

^{1}H NMR (400 MHz, D_2O-buffer, pH 10): δ 3.01 (t, *J* = 5.4 Hz, **5**), 3.04 (t, *J* = 5.7 Hz, **2**), 3.16 (t, *J* = 5.4-5.7 Hz, unknown D), 3.19 (t, *J* = 5.4-6.0 Hz, **3**), 3.61 (t, *J* = 5.7 Hz, unknown D), 3.66 (t, *J* = 5.7 Hz, **2**), 3.71 (t, *J* = 5.4-6.0 Hz, **3**), 3.76 (t, 5.4 Hz, **5**), 3.92 (s, **2**), 4.16 (s, **3**), 4.26 (s, **2**), 4.49 (s, **3**).

^{13}C NMR (100 MHz, D_2O): δ 35.1 (**3**), 44.7 (**5**), 46.0 (unknown D), 53.0 (**3**), 56.7 (**2**), 57.5 (**2**), 60.1 (**3**), 61.0 (**3**), 61.5 (**2**), 63.7 (**5**), 64.1 (unknown D), 76.4 (**2**).

Another ^{1}H NMR spectrum was recorded after seven days, and this spectrum contained only the signals of **5** and unknown D in addition to the four new signals that are assigned to **3**.

9.5.2 Triazinane 1 and Two Equivalents of HS^-

Triazinane **1** (70 %, 0.010 g, 0.032 mmol) was dissolved in a D_2O-buffer of pH 10.0. Na_2S (60 %, 0.012 g, 0.092 mmol) was added and the reaction was followed by ^{1}H NMR. The spectra recorded after 24 hours and after four days contained the same signals as the ones given Section 9.5.1, though with different intensities.

9.5.3 Separation and Isolation of the Product

Liquid/Liquid Extraction

Triazinane **1** (70 %, 1.0 g, 3.2 mmol) and Na_2S (60 %, 1.2 g, 9.5 mmol) were mixed in a buffered, aqueous solution of pH 10.0 (100 ml). The reaction mixture was kept at a constant pH for five hours, when a ^1H NMR spectrum showed that thiadiazinane **2** was the dominant component in the solution, in addition to **5**. Another equivalent of Na_2S (60 %, 0.58 g, 4.5 mmol) was added to complete the reaction. After 24 hours, another ^1H NMR spectrum showed that the relative amounts of **2** and **3** were 1:1. The reaction mixture was kept at a constant pH for another 24 hours, when ^1H NMR spectrum showed that the amount of **3** in the solution was more than six times greater than the amount of **2**. **3** was continuously extracted from the reaction mixture with dichloromethane for one hour. ^1H NMR of the aqueous phase showed that no **3** was left in the reaction mixture. The solvent was evaporated from the organic phase. ^1H NMR analysis ($CDCl_3$) of the isolated product showed that the purity of **3** was 98 %, the only contaminant being dichloromethane.

Short Path Distillation

The short path distillation apparatus was evacuated. Solid carbon dioxide (dry ice) was used to cool and condense any vapour formed in the experiments.

In the attempt to separate **2** and **3** by short path distillation, several mixtures of pure **2** and **3** from the liquid-liquid extraction experiments (Section 4.2.1) were combined in dichloromethane, which was then evaporated to yield a mixture that from ^1H NMR spectroscopy contained mainly **2** and **3**, but also small amounts of **1** and **5**. The mixture was put in a short path distillation apparatus which was evacuated to 1.8×10^{-4} atm. The temperature was increased from room temperature to 200°C. The mixture gradually turned brown, but no boiling was observed. ^1H NMR analysis after the experiment showed that **3** was intact, whereas **1** and **2** had decomposed. The relative amount of **5** had increased. Some new signals with low intensity were also observed in the spectrum.

9.5.4 Analyses of Dithiazinane 3

Dithiazinane **3** with a purity of 98 % was synthesized and isolated as described in Section 9.5.3.

Mass Analysis

Elemental analysis was performed on the isolated **3**.

Anal. Calcd. for $C_5H_{11}NOS_2$: C, 36.3; H, 6.7; N, 8.5; S, 38.8. Found: C, 35.7; H, 6.5; N, 8.4; S, 37.2.

Low Temperature ^{1}H NMR spectra

Dithazinane **3** was analysed by ^{1}H NMR spectroscopy at room temperature, -15 °C, -40 °C, -53 °C, -66 °C, and -79 °C. The ^{1}H NMR data for room temperature and -79 °C are given below.

^{1}H NMR (400 MHz, D_2O, 23 °C): δ 3.16 (t, *J* = 5.7-5.8 Hz), 3.63 (t, *J* = 5.7-5.8 Hz), 4.12 (s), 4.48 (s).

^{1}H NMR (400 MHz, D_2O, -79 °C): δ 3.15 (t, *J* = 5.5-5.6 Hz), 3.62 (t, *J* = 5.5-5.7 Hz), 3.62 (d), 4.08 (d, *J* = 13.1 Hz), 4.67 (d, *J* = 13.5 Hz), 4.92 (d, *J* = 13.3 Hz).

IR Spectroscopy

IR (neat): ν/cm^{-1} 3394 (s), 2915 (s), 1429 (s), 1283 (s), 1195 (m), 1059 (s), 941 (m), 873 (m), 728 (m), 689 (m), 668 (w).

9.5.5 Triazinane 1 and Large Excess of HS^-

*Triazinane **1** and Three Equivalents of HS^-*

Triazinane **1** (70 %, 0.010 g, 0.032 mmol) was dissolved in a D_2O-buffer of pH 10 (10.0 ml), and NaHS (68 %, 0.011 g, 0.13 mmol) was added. After 22 hours, a ^{1}H NMR spectrum was recorded, showing that the ratio between **2** and **3** was 1:0.9. The reaction was left for another six days, after which another ^{1}H NMR analysis showed that the reaction mixture contained **3**, **5**, and the unknown compound D (Section 4.1.5). No new signals were found in the spectrum, and no change was observed in the reaction mixture.

*Triazinane **1** and Five Equivalents of HS^-*

Triazinane **1** (70 %, 0.10 g, 0.32 mmol) was dissolved in an aqueous, buffered solution of pH 10.0 (50.0 ml), and Na_2S (60 %, 0.29 g, 2.2 mmol) was added. The pH was lowered to 8.0 to get the reaction started. The pH increased steadily as the reaction proceeded. The reaction was followed by ^{1}H NMR spectroscopy. After 2.5 hours, the ratio between **2** and **3** was 1:1.3. The reaction was left for seven weeks for completion. The pH was adjusted to 10.0 with aqueous

HCl three times during this period. After seven weeks, a white solid was observed in the mixture. The ^{1}H NMR spectrum now only contained the signals from **3**, **5**, and unknown D. The solid was too fine to be separated from the mixture by filtration, so centrifugation was used for the separation. The solid was washed with water and dried.

Unsuccessful attempts were made to dissolve the solid in water, methanol, dichloromethane, DMSO and hexane. Attempts were also made to record ^{1}H NMR spectra of the solid by dissolving it in deuterated water, chloroform and DMSO, but not enough matter was dissolved to get acceptable spectra.

The solid was also analysed by IR spectroscopy, but the quality of the spectra were bad and indicated that the solid was not uniform.

Attempts to measure the melting point of the solid failed. A part of the solid sublimed at 110°C. The rest gradually turned brown as the temperature was raised.

*Dithiazinane **3** and Four Equivalents of HS^-*

Dithiazinane **3** (0.050 g, 0.30 mmol) was dissolved in an aqueous, buffered solution of pH 8.0 (10.0 ml), and Na_2S (60 %, 0.076 g, 0.58 mmol) was added. ^{1}H NMR spectra recorded after one hour and after 20 hours contained only the signals from **3**. The pH was lowered to 6.0 by addition of aqueous HCl. Acetonitrile (0.012 g, 0.31 mmol) was added as an internal standard. After three hours at pH 6.0, ^{1}H NMR analysis showed that no change had occurred in the solution. The pH was lowered to 2.0 by addition of concentrated HCl. After another 20 hours no change or precipitation of solid was observed in the reaction mixture, and another two equivalents of Na_2S (60 %, 0.076 g, 0.58 mmol) was added to the solution. Four hours later, a ^{1}H NMR analysis showed that the ratio between **3** and the IS was still 1:1.

9.5.6 Triazinane 1 and Gaseous H_2S

Triazinane **1** (70 %, 0.55 g, 1.8 mmol) and acetonitrile (IS, 0.10 g, 2.5 mmol) was dissolved in water (50.0 ml). Gaseous H_2S was bubbled through the solution for 2.5 minutes. A ^{1}H NMR spectrum was recorded of the reaction mixture.

^{1}H NMR (300 MHz, D_2O): δ 2.07 (s, IS), 3.14 (t, *J* = 5.2-5.3 Hz, **5**), 3.19 (t, *J* = 5.6-5.8 Hz, **3**), 3.71 (t, *J* = 5.5-5.8 Hz, **3**), 3.82 (t, *J* = 5.2-5.3 Hz, **5**), 4.16 (s,

3), 4.49 (s, **3**). Traces: δ 2.91 (t, *J* = 5.4-5.7 Hz, **1**), 3.04 (t, *J* = 5.7-6.1 Hz, **2**), 3.61 (t, *J* = 5.9 Hz, unknown D), 3.92 (s, **2**), 4.26 (s, **2**).

9.6 The Rate of the Reaction between Triazinane 1 and HS^-

9.6.1 Method for Determination of Sulfide

The First Attempt

Triazinane **1** (70 %, 1.0 g, 3.2 mmol) were dissolved in a buffer of pH 9.0 (50.0 ml), and Na_2S (60 %, 0.058 g, 0.45 mmol) was added. After the reactants were dissolved, the pH was 9.98. During the reaction, the pH decreased and reached 9.50 after 13 minutes. Samples of 1.00 ml was taken from the reaction mixture every two minutes, diluted with water (4.00 ml) and the buffered stabilizing solution (5.00 ml). For each sample, the voltage was recorded 30 seconds after the dilution took place. Voltages were then recorded 60 seconds, 90 seconds, and 120 seconds after the dilution. The recorded voltages increased during this time, and the values were extrapolated to give the voltage at the time of the dilution. The sulfide concentration was found from the calibration curve that was made the same day.

The experiment described above was repeated. The decrease in pH was half a unit after 13 minutes. It was attempted to calibrate the electrode on the same day, but very unstable readings were recorded, and the calibration curve from the previous experiment, made the previous day, was used.

The Second Attempt

Triazinane **1** (0.50 g, 1.6 mmol) was dissolved in a buffered water solution of pH 9.8 (25.0 ml) and the pH was adjusted to 10.0 with solid K_2CO_3. NaHS (72 %, 0.0093 g, 0.23 mmol) was dissolved in the same buffer (25.0 ml) and the pH was adjusted to 9.96 with solid K_2CO_3. The two solutions were mixed and after that the voltage were recorded every 30 seconds. The experiment was reproduced.

In a third performance of the experiment, Na_2S (60 %, 0.029 g, 0.22 mmol) replaced NaHS, **1** was dissolved in 10.0 ml of the buffer, and Na_2S was dissolved in 40.0 ml of the buffer. Otherwise, the experiment was performed in the same way.

Reproducibility Tests of Sulfide Electrode

Na_2S (60 %, 0.029 g, 0.22 mmol) was dissolved in a buffered aqueous solution of pH 10.0 (50.0 ml). The voltage was recorded every five minutes for 65 minutes, and during that time, five iodometric titrations were performed. The found sulfide concentrations were 0.066 M (0 minutes), 0.066 M (5 minutes), 0.065 M (20 minutes), 0.059 M (40 minutes) and 0.063 M (65 minutes).

Na_2S (60 %, 0.029 g, 0.22 mmol) was dissolved in water (5.00 ml). This was done three times, yielding three solutions. They were immediately analysed with the sulfide-sensitive electrode in the same order as they were made. The voltages were 890.0, 887.5 and 885.1 mV for samples 1, 2 and 3, respectively. The samples were also titrated with I_2, and the sulfide concentration was calculated to be 0.047, 0.047 and 0.048 M, respectively.

Three days later, a fourth sample was made in the same way as the other samples. This sample had a voltage of 897.7 mV and a sulfide concentration of 0.047 M from iodometric titration.

9.6.2 Method for Determination of Triazinane

The Reactivity of Triazinane 1

Three solutions were made as described below.

Solution 1: Triazinane **1** (70 %, 0.078 g, 0.25 mmol) and acetonitrile (IS, 0.0103 g, 0.25 mmol) were dissolved in D_2O (5.00 ml).

Solution 2: NaHS (68 %, 0.20 g, 2.4 mmol) was dissolved in D_2O (5.00 ml).

Solution 3: A 0.50 M solution of Na_2HPO_4 in D_2O.

The pH was adjusted to 11.0 in all three solutions. 0.10 ml of solution 1 and 0.80 ml of solution 3 were transferred to an NMR-tube with a syringe. The time was started as 0.10 ml of solution 2 was added to the tube, which was shaken and immediately put into the NMR instrument. After 1.5 minutes, a two-minute ^1H NMR spectrum was recorded. This spectrum gave the composition of the reaction mixture after 2.5 minutes. After this, spectra were automatically recorded every two minutes (t = 4.5 minutes, 6.5 minutes etc.).

When all the spectra at pH 11.0 had been recorded, the pH was adjusted to 10.5 in the same three solutions. The experiment was performed in the same way,

but spectra were recorded every minute and the first one was recorded at t = 3.5 minutes.

When all the spectra at pH 10.5 had been recorded, the pH was adjusted to 10.0 in the three solutions. This experiment was performed in the same way as the previous, and the first spectrum was recorded at t = 2.5 minutes.

9.7 Stability and Reactivity of Other 1,3,5-Triazinanes

9.7.1 1,3,5-Triethyl-1,3,5-triazinane

Rate of Hydrolysis

The experiment was performed as described in Section 9.3.2 for the experiment performed at 22 °C, with a 5 % solution of triazinane **8** as a stock solution. The buffer solutions of pH 10.0, 9.0 and 8.0 were made and used in the experiment.

Reaction Products with H_2S:

NaHS (68 %, 0.80 g, 9.7 mmol) was mixed with 1,3,5-triethyl-1,3,5-triazinane (**8**, 39 wt%, 2.200 g, 5.00 mmol) and the mixture was diluted to 10.0 ml with 0.50 M Na_2HPO_4. The pH was adjusted to 10.0.

In the control experiment, **8** (39 wt%, 0.22 g, 0.50 mmol) and Na_2S (60 %, 0.063 g, 0.48 mmol) were dissolved in an aqueous buffer of pH 9.0. The pH was adjusted to 10.0.

In another experiment, triazinane **8** (39 wt%, 1.100 g, 2.50 mmol) and acetonitrile (IS, 0.315 g, 7.67 mmol) were mixed and diluted to 50.0 ml with water. H_2S-gas was bubbled through the solution for 10 minutes.

Rate of Reaction with H_2S:

The experiment was performed as described in Section 9.6.2, and the solutions used were:

Solution 1: Triazinane **8** (39 wt%, 0.10 g, 0.25 mmol) and acetonitrile (IS, 0.01 g, 0.26 mmol) was dissolved in D_2O (5.00 ml).

Solution 2: Na_2S (60 %, 0.314 g, 2.41 mmol) was dissolved in D_2O (5.00 ml).

Solution 3: A 0.50 M solution of Na_2HPO_4 in D_2O.

The experiments were performed at pH 11.0, 10.5 and 10.0. The spectra were recorded with intervals of two minutes.

9.7.2 1,3,5-Trimethyl-1,3,5-triazinane

Rate of Hydrolysis

The experiment was performed as described in Section 9.3.2 for the experiment performed at 22 °C, with a 5 % solution of triazinane **9** as a stock solution. The buffer solutions of pH 10.0, 9.0 and 8.0 were made and used in the experiment. An additional experiment was performed, using the same procedure and a buffer of pH 7.5 (0.50 M Na_2HPO_4 acidified to pH 7.5).

Reaction Products with H_2S:

NaHS (68 %, 0.80 g, 9.7 mmol) was mixed with 1,3,5-trimethyl-1,3,5-triazinane (**9**, 38 wt%, 1.7 g, 5.0 mmol) and the mixture was diluted to 10.0 ml with 0.50 M Na_2HPO_4. The pH was adjusted to 10.0. After three days, the formed crystals were filtrated off and washed with water. The crystals were analysed by ^1H and ^{13}C NMR, and EIMS and HRMS.

^1H NMR (400 MHz, $CDCl_3$): δ 2.69 (s, N-C$\underline{H}_3$), 4.09 (s, N-C$\underline{H}_2$-S), 4.42 (s, S-C$\underline{H}_2$-S).

^{13}C NMR (400 MHz, $CDCl_3$): δ 60.0 (N-$\underline{C}H_3$), 37.6 (N-$\underline{C}H_2$-S), 34.4 (S-$\underline{C}H_2$-S).

EIMS (70eV) *m/z* (rel.int.%): 137.1 (M+2, 1.4), 135.1 (M^+, 16), 89.0 (9), 70.1 (2), 57.1 (18), 46.0 (4), 45.0 (4), 44.0 (18), 43.0 (3), 42.0 (12), 41.0 (1).

HRMS (70eV) *m/z*: Observed 135.01765, calculated 135.01771.

In the same manner as for triazinane **8**, triazinane **9** (38 wt%, 0.850 g, 2.50 mmol) and acetonitrile (IS, 0.103 g, 2.50 mmol) were mixed and diluted to 50.0 ml with water. H_2S-gas was bubbled through the solution for 23 minutes.

Rate of Reaction with H_2S:

The experiment was performed as described in Section 9.6.2, and the solutions used were:

Solution 1: Triazinane **9** (38 wt%, 0.085 g, 0.25 mmol) and acetonitrile (IS, 0.0103 g, 0.250 mmol) were dissolved in D_2O (5.00 ml).

Solution 2: Na_2S (60 %, 0.314 g, 2.41 mmol) was dissolved in D_2O (5.00 ml).

Solution 3: A 0.50 M solution of Na_2HPO_4 in D_2O.

The experiments were performed at pH 11.0, 10.5 and 10.0. The spectra were recorded with intervals of 2.5 minutes.

9.7.3 2,4,6-Trimethyl-1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane

Acetaldehyde (1.27 g, 0.030mol) was added to pure ethanolamine (**5**, 1.80 g, 0.029 mol) over 5 minutes. The reaction mixture was kept in an ice bath.

9.8 Stability and Reactivity of Trioxanes, Tetroxanes and an Oxolane

9.8.1 1,3,5-Trioxane

In the reaction at pH 10.0, 1,3,5-trioxane (**20**, 0.23 g, 2.5 mmol) was dissolved in a buffer (50.0 ml), and Na_2S (60 %, 0.32 g, 2.5 mmol) was added. The pH was adjusted to 10.0.

At the same time, formaldehyde dihydrate (37 %, 0.19 g, 2.5 mmol) was dissolved in a buffer (50.0 ml), and Na_2S (60 %, 0.32 g, 2.5 mmol) was added. The pH was adjusted to 10.0.

In the experiment at pH 7.0, **20** (0.23 g, 2.5 mmol) was dissolved in water (25.0 ml), and NaHS (68 %, 0.20 g, 2.4 mmol) was added. The pH was adjusted to 7.0.

The stability test was performed by dissolving trioxane **20** (0.015 g, 0.17 mmol) in D_2O (3.0 ml). The solution was measured into three containers of 1.0 ml each. Container 1 was left without adjusting the pH, which was 5.5 by pH paper. In container 2, the pH was adjusted to 2.5, and in container 3 to 1.5.

Finally, trioxane **20** (0.23 g, 2.5 mmol) and acetonitrile (IS, 0.10 g, 2.5 mmol) were dissolved in water (50.0 ml) and gaseous H_2S was bubbled through the solution for 25 minutes. The pH in the solution was 5 by pH paper when the supply of H_2S was stopped.

9.8.2 2,4,6-Trimethyl-1,3,5-trioxane

2,4,6-Trimethyl-1,3,5-trioxane (**21**, 0.33 g, 2.5 mmol) was dissolved in water (50.0 ml). NaHS (68 %, 0.20 g, 2.4 mmol) was added, and the pH was adjusted to 10.0. ^{1}H NMR spectra were recorded after three hours and after three days. The pH was lowered to 7.0 and another ^{1}H NMR spectrum was recorded one day later.

Trioxane **21** was reacted with H_2S by bubbling the gas through a solution of **21** (0.33 g, 2.5 mmol) and acetonitrile (IS, 0.10 g, 2.5 mmol) in water (50.0 ml) for 20 minutes. ^{1}H NMR spectra were recorded before the reaction and two hours after the gas supply was stopped.

9.8.3 1,3,5,7-Tetroxane

The attempt to synthesize the paraformaldehyde diacetate (**24**) was performed by mixing paraformaldehyde (**23**, 2.5 g) and acetic anhydride (0.85 g, 0.083 mol) in an autoclave. The autoclave was closed, and a magnetic stirrer was used as the temperature was raised to, and kept at, 160 °C for 23 hours. The reactor was allowed to reach room temperature before it was opened. Some of the sublimed matter (1.5 g) was isolated and washed with diethyl ether (2x10 ml) and ethyl acetate (10 ml).

The solid isolated in the previous experiment (1.01 g) was placed in a round-bottomed flask with sodium persulfate ($Na_2S_2O_8$, 0.030 g, 0.25 mmol). The flask was connected to a long glass tube, which in turn was connected to two cold traps at -78°C. The system was evacuated, and the flask was heated to 160 °C. After 2.5 hours, no product was observed in the cold traps.

Another attempt was made to synthesize tetroxane (**26**). The paraformaldehyde (12.5 g) and the acetic anhydride (4.25 g, 0.042 mol) were placed in the autoclave and heated to 160 °C for 21 hours. The sublimed matter (5.85 g) was washed with diethyl ether (3x10 ml) and ethyl acetate (3x10 ml). In the next step, the solid (0.50 g) and the acid catalyst ($Na_2S_2O_8$, 0.030 g, 0.25 mmol) was mixed and crushed, and placed in a standard sublimator, in which the sublimed product would only have to travel a short distance to the cold finger. The cold finger was cooled to -10 °C. The bottom of the sublimator was heated to 180 °C. No solid deposited on the cold finger after 7 hours.

A third attempt was performed as described in the second attempt, but $K_2S_2O_8$ (0.030 g, 0.11 mmol) replaced $Na_2S_2O_8$ as the acid catalyst. Again, no solid deposited on the cold finger.

9.8.4 1,3-Dioxolane

Gaseous H_2S was bubbled through a solution of 1,3-dioxolane (**26**, 0.181 g, 2.44 mmol) and acetonitrile (IS, 0.109 g, 2.65 mmol) in water (50.0 ml). The experiment was stopped after five minutes, and the pH in the solution was 4 by pH paper.

In the second experiment, **26** (0.182 g, 2.46 mmol) and the IS (0.112 g, 2.73 mmol) were dissolved in water (50.0 ml), and H_2S was bubbled through the solution for 35 minutes. No change was obsreved in the ^1H NMR spectrum.

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APPENDIXES

Appendix A

NMR Data for Pure Compounds

Appendix A

*1,3,5-Tris(2-hydroxyethyl)-1,3,5-triazinane (**1**):*

^{1}H NMR (300 MHz, D_2O): δ 2.69 (t, *J* = 5.8 Hz, N-C$\underline{H}_2$-CH_2-OH), 3.49 (br. s, N-C$\underline{H}_2$-N), 3.70 (t, *J* = 5.8 Hz, N-CH_2-C$\underline{H}_2$-OH).

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.65 (t, *J* = 4.9-5.3 Hz, N-C$\underline{H}_2$-CH_2-OH), 3.50 (br. s, N-C$\underline{H}_2$-N), 3.68 (t, *J* = 4.9-5.3 Hz, N-CH_2-C$\underline{H}_2$-OH).

^{13}C NMR (75 MHz, D_2O): δ 56.5 (N-$\underline{C}H_2$-CH_2-OH), 60.0 (N-CH_2-$\underline{C}H_2$-OH), 75.7 (N-$\underline{C}H_2$-N).

*2-Aminoethanol/ethanolamine (**5**):*

^{1}H NMR (300 MHz, D_2O): δ 2.73 (t, *J* = 5.6 Hz, N-C$\underline{H}_2$-CH_2-OH), 3.61 (t, *J* = 5.6 Hz, N-CH_2-C$\underline{H}_2$-OH).

^{1}H NMR (300 MHz, D_2O-buffer, pH 10): δ 2.83 (t, *J* = 5.5 Hz, N-C$\underline{H}_2$-CH_2-OH), 3.67 (t, *J* = 5.4-5.6 Hz, N-CH_2-C$\underline{H}_2$-OH).

^{13}C NMR (75 MHz, D_2O): δ 45.2 (N-$\underline{C}H_2$-CH_2-OH), 65.2 (N-CH_2-$\underline{C}H_2$-OH).

Aqueous formaldehyde:

^{1}H NMR (400 MHz, D_2O): δ 4.83 (s, HO-C$\underline{H}_2$-OH).

^{13}C NMR (100 MHz, D_2O): δ 84.6 (s, HO-$\underline{C}H_2$-OH).

*2-mercapto-ethanol (**6**):*

^{1}H NMR (300 MHz, D_2O): δ 2.69 (t, *J* = 6.1-6.3 Hz, HS-C$\underline{H}_2$-CH_2-OH), 3.71 (t, *J* = 6.1-6.2 Hz, HS-CH_2-C$\underline{H}_2$-OH).

^{1}H NMR (300 MHz, D_2O-buffer, pH 10): δ 2.66 (t, *J* = 6.8 Hz, HS-C$\underline{H}_2$-CH_2-OH), δ 3.65 (t, *J* = 6.8 Hz, HS-CH_2-C$\underline{H}_2$-OH).

^{13}C NMR (75 MHz, D_2O-buffer, pH 10): δ 28.8, 66.4.

*1,3,5-Trithiane (**4**):*

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.33 (s).

Melting point: 215-216°C.

*1,3,5-triethyl-1,3,5-triazinane (**8**):*

^{1}H NMR (300 MHz, D_2O): δ 1.07 (t, *J* = 7.2 Hz, N-CH_2-C<u>H</u>$_3$), 2.55 (q, *J* = 7.2-7.5 Hz, N-C<u>H</u>$_2$-CH_3), 3.38 (br. s, N-C<u>H</u>$_2$-N).

^{13}C NMR (100 MHz, D_2O): δ 13.6 (N-CH_2-<u>C</u>H_3), 49.0 (N-<u>C</u>H_2-CH_3), 74.1 (N-<u>C</u>H_2-N).

*1,3,5-Trimethyl-1,3,5-triazinane (**9**):*

^{1}H NMR (300 MHz, D_2O): δ 2.27 (s, N-C<u>H</u>$_3$). The signal from the ring protons is barely visible at δ 3.4 ppm.

^{13}C NMR (75 MHz, D_2O): δ 41.8 (N-<u>C</u>H_3), 77.5 (N-<u>C</u>H_2-N).

*1,3,5-Trioxane (**19**):*

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.16 (s).

^{13}C NMR (75 MHz, $CDCl_3$): δ 93.6.

^{1}H NMR (300 MHz, D_2O): δ 5.24 (s).

^{13}C NMR (75 MHz, D_2O): δ 96.4.

*2,4,6-Trimethyl-1,3,5-trioxane (**20**):*

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.39 (d, *J* = 5.4 Hz, CH-C<u>H</u>$_3$), 5.04 (q, *J* = 5.1 Hz, C<u>H</u>-CH_3).

^{1}H NMR (300 MHz, D_2O): δ 1.36 (d, *J* = 5.1 Hz, CH-C<u>H</u>$_3$), 5.27 (q, *J* = 5.1-5.4 Hz, C<u>H</u>-CH_3).

^{1}H NMR (300 MHz, D_2O, pH 10): δ 1.37 (d, *J* = 5.1 Hz, CH-C<u>H</u>$_3$), 5.28 (q, *J* = 5.1-5.4 Hz, C<u>H</u>-CH_3).

Acetaldehyde:

^{1}H NMR (300 MHz, D_2O): δ 1.33 (d, *J* = 5.4 Hz, C<u>H</u>$_3$-$CH(OH)_2$), 2.24 (d, *J* = 3.0 Hz, C<u>H</u>$_3$-CHO), 5.24 (q, *J* = 5.1-5.4 Hz, CH_3-C<u>H</u>$(OH)_2$), 9.67 (q, *J* = 3.0 Hz, CH_3-C<u>H</u>O).

*1,3-Dioxolane (**25**):*

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (s), 4.91 (s).

^{13}C NMR (100 MHz, $CDCl_3$): δ 64.6, 95.1.

^{1}H NMR (400 MHz, D_2O): δ 3.93 (s), 4.90 (s).

^{13}C NMR (100 MHz, D_2O): δ 67.1, 97.0.

*Ethyleneglycol (**26**):*

^{13}C NMR (75 MHz, D_2O): δ 65.4.

Appendix B

Equations for Calculation of Uncertainties

Appendix B

In this work, two statistical methods have been applied in order to establish the relationship between variables and estimate the uncertainty: Simple linear regression[24] and error propagation[25].

B.1 Simple linear regression

Two variables, Y and x, are assumed to have a linear relationship. When several experimental points for the variables Y and x are available, a line to best fit can be generated using the Method of Least Squares (MLS). The regressed line will satisfy equation B-1.

$$Y = \alpha + \beta x \tag{B-1}$$

Above, α and β are unknown intercept and slope parameters respectively.

Each experimental point i will satisfy the equation

$$Y_i = \alpha + \beta x_i + \varepsilon_i \tag{B-2}$$

where ε_i is the distance from Y_i to the regression line. MLS generates a regression line in which the sum of the square errors ε_i (SSE) is minimized. SSE for n measurements is defined in equation B-3:

$$SSE = \sum_{i=1}^{n} \varepsilon_i^2 \tag{B-3}$$

The standard deviation *s* in the regression is

$$s^2 = \frac{\sum_{i=1} \varepsilon_i^2}{n-2} \tag{B-4}$$

Applying Microsoft Excel 1997, the statistical program used in this work, the parameters α, β and *s* are automatically calculated.

B.2 Error propagation

In linear regression, the experimental error in the variables Y and x is often neglected, and the overall deviation in the results are represented by the regression error expressed in equation B-4. However, many parameters are determined through mathematical expressions in which the experimental errors in the variables are highly significant. Assuming that the parameter y is determined from the following expression

$$y = f(x_1, x_2, \ldots, x_p) \tag{B-5}$$

the uncertainty in y, s_y can be estimated by equation B-6.

$$s_y^2 = \sum_{i=1}^{p} \left(\frac{\partial f}{\partial x_i}\right)^2 s_{x_i}^2 \tag{B-6}$$