THE UNIVERSITY OF CALGARY

STUDIES ON THE THERMAL DECOMPOSITION OF ORGANIC POLYSULPHANES

by

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled, "Studies on the Thermal Decomposition of Organic Polysulphanes" submitted by Christopher O. Oriakhi in partial fulfillment of the requirements for the degree of Master of Science.

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ABSTRACT

The thermal decomposition of dimethyl and *bis*(methylphenyl) polysulphanes $[CH_3S_xCH_3 \text{ and } (CH_3C_6H_4)_2S_x]$ have been investigated both in open and closed reactor systems, with the goal of determining their stability and the products of their decomposition between 50° and 150°C, as well as obtaining kinetic and mechanistic information that may be helpful in explaining the observed decomposition.

Dimethyl polysulphane (DMPS) was observed to exhibit different decomposition behaviour in the open and closed systems. Analysis using HPLC, GC-MS, and ¹H and ¹³C NMR indicated that the main products of the decomposition of DMPS were methanethiol (CH₃SH) and carbon disulphide (CS₂) in the open and closed system as well as CS₂ and H₂S in the closed system. The CH₃SH produced in the closed system experiments is thought to have undergone secondary reactions yielding H₂S and reforming DMPS and dimethyl disulphane (DMDS). The rate of formation of CH₃SH from DMPS in the open system was determined and it was observed that all data fitted the first order rate expression. A plot of log k versus 1/T for rate constants obtained at various temperatures gave energy of activation for the formation of methanethiol in an open system as 52.80 ± 4.34 kJmol⁻¹. Additional influence of the percent sulphur loading (i.e. value of x in CH₃S_XCH₃) on the rate of decomposition of DMPS in the open system was examined and found to have a complex effect on the rate of methanethiol formation in an open system.

The addition of hydrogen sulphide in varying proportion was found to inhibit the decomposition of DMPS in the closed system to a large extent whereas extensive decomposition of DMPS was observed in the closed system without H_2S . Possible mechanisms for the observed decomposition under the various experimental conditions are discussed.

Bis(methylphenyl) polysulphane exhibited a remarkable stability over dimethyl polysulphane and did not show any evidence of decomposition at 150° and 200° C over a reaction time of 15 days both in the presence and absence of H₂S. The enhanced stability of *bis*(methylphenyl) polysulphane is discussed and the possibility of utilizing dimethyl and/or diaryl disulphane to mitigate sulphur deposition problems when producing high H₂S containing natural gas reservoirs is discussed.

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#### CHAPTER ONE

#### **INTRODUCTION**

#### 1.1 Some General Considerations

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Polysulphanes are chemical compounds containing cumulated sulphur-sulphur bonds with terminal organic or inorganic groups. This dissertation is concerned primarily with organic polysulphanes of the type  $RS_xR$ , where R is an alkyl or aryl group and x is the number of sulphur atoms. Organic polysulphanes of various types are known, and in all cases their chemistry differs greatly from that of monosulphanes and disulphanes.

There are several methods for preparing organic polysulphanes. Among the earliest known methods is the reaction of thiols with sulphur halides [1].

$$2C_2H_5SH + SCl_2 \longrightarrow C_2H_5SSSC_2H_5 + 2HCl$$
 (1)

 $2C_2H_5SH + S_2Cl_2 \longrightarrow C_2H_5SSSSC_2H_5 + 2HCl$ (2)

Specifically, tetrasulphanes may be prepared [2] from alkali tetrasulphides and alkyl or aryl halides:

 $2RCl + Na_2S_4 \qquad \longrightarrow \qquad RSSSSR + 2NaCl \qquad (3)$ 

or by the oxidation of alkyl hydrogen disulphane:

 $2RSSH + I_2 \longrightarrow RSSSSR + 2HI$ (4)

Polysulphanes have also been made by the addition of elemental sulphur to a disulphane in the presence of an amine or a hydrosulphide catalyst [2,3,4].



This method is useful when polysulphanes with x > 4 are required. These methods often yield mixtures of polysulphanes which are difficult to separate and purify when the number of sulphur atoms per chain is more than three. In fact individual tetrasulphanes and the higher polysulphanes are difficult to isolate, purify and characterize due to their low stability [5,6]. For example, all attempts to purify dimethyl pentasulphane by distillation have resulted in the formation of dimethyl trisulphane and disproportionation products [7].

Many uses for organic polysulphanes have been suggested [1]. A major industrial application of organic polysulphanes is in the vulcanization of rubber where they find use as sulphur donors. Vulcanization is simply the conversion of natural or synthetic rubber molecules into a cross-linked network. This may be achieved by the use of vulcanizing agents such as sulphur, polysulphanes and peroxides. The attractive property of organic polysulphanes for this application is their thermal instability. They readily liberate sulphur at the vulcanization temperature (which depends on the type of rubber, but is usually in the range of 140° to 240°C) [8]. The advantage of using polysulphanes rather than elemental sulphur in cross-linking of rubber is that they serve as both a vulcanizing agent. The following equations depict the vulcanizing action of a polysulphane:



Figure 1.1 Vulcanization of Rubber Using Polysulphanes

Alkyl polysulphanes have been used as polymerization initiators and in the synthesis of polysulphane elastomers [9,10]. In general the chemistry of organic polysulphanes is extensive and has been reviewed several times [1,2,6,11-12].

#### 1.2 Use Of Organic Di- and Polysulphanes in Sour Gas Production

Sour gas is a natural gas containing hydrogen sulphide  $(H_2S)$  in the range of a few parts per million (ppm) to 97% and is found in Alberta and in different parts of the world (Table 1.1). Until 1950, the world supply of elemental sulphur came primarily from Frasch mining, that is, the mining of native sulphur deposits [13]. However, the last four decades has witnessed a remarkable growth in the recovery of sulphur from the

### Table 1.1

### Some Sour Gas Fields Around the World

J	Location	% H ₂ S Content
Canada	(Bearberry, Alberta)	90
	(Panther River, Alberta)	70 - 80
	(Harmattan)	53.5
China	(Zhaolanzhuang)	60 - 90
USSR	(Astrakhan)	22.5 ·
USA	(Murray Franklin, Texas)	98
	(Eustace, East Texas)	85 <b>-</b> 90
	(Josephine, Mississippi)	78
	(Cox, Mississippi)	65
France	(Lacq)	16
W. Germany	(Varnhorn)	22.4

hydrogen sulphide content of natural and refinery gases. As a result of the major sour gas developments in France, Western Canada, and the United States of America in the 1950's and 1970's, the role of Frasch mined sulphur in the market place has diminished although it still supplies about 26% of the world sulphur [13].

One of the major problems facing the sour natural gas producing industry is the deposition of elemental sulphur in production facilities. Originally, this sulphur is in solution in the reservoir fluid, but, production of the gas and the resulting drop in the temperature and pressure of the fluids causes the sulphur to come out of solution. These phenomena have been examined extensively by Hyne and his co-workers [14-15]. Organic disulphane solvents are being used by field operators in the Canadian and United States sour gas industries to mitigate this problem of sulphur deposition. About 3 - 5 weight percent of an amine or a hydrosulphide catalyst is usually added to the disulphane solvent to initiate the uptake of sulphur. Polysulphane formation is the result of sulphur uptake by the disulphane solvents.

Clark and co-workers [16] have proposed a mechanism for the chemical uptake of elemental sulphur by the disulphane solvent (Figure 1.2). The polysulphane formed is also a good physical solvent for sulphur, that is, it dissolves sulphur without chemically reacting with it. This may be due to the similarities in their molecular structures:



Since the molecular structure of a molecule determines its polarity, the polysulphane molecules should be able to solvate and hence dissolve elemental sulphur. The major drawback to the use of organic disulphane solvents in high hydrogen sulphide containing





reservoirs (super sour gas wells higher than 55%  $H_2S$ ) is that they have traditionally been used in batch treatments. Since these organic solvents are relatively expensive, there is the need to regenerate and recirculate spent solvents. Some regeneration methods have been developed recently [17].

#### 1.3 A Review of Some Important Aspects of Polysulphane Chemistry

The thermal decomposition of organic polysulphanes has been an area of interest in connection with the nature of the sulphur-sulphur bonds. The accumulated body of evidence from bond dissociation energy studies, thermochemical bond energy studies and *ab initio* molecular orbital calculations available in the literature suggests that organic polysulphanes are unstable with respect to S-S bond cleavage [18-22].

Studies have been reported [18,20,24-28] which attempt to provide a quantitative measure of the differences in strength between disulphane and polysulphane S-S linkages. Some representative results are given in Table 1.2. It is clear that polysulphane linkages are weaker than the disulphane linkages and that the energy required per homolytic cleavage of the S-S bond decreases with the increasing number of sulphur atoms per chain [6,12,23]. This accounts for the relative instability of organic polysulphanes.

The thermal disproportionation of large organic polysulphanes to smaller and larger polysulphanes has been studied extensively. For example, Bloomfield investigated the thermal decomposition of diphenyl tetrasulphane and its contributions to the sulphur-olefin reaction [31]. At temperatures in the region of 140°C, it was suggested that the polysulphane breakdown involved the rupture of the S-S bonds. The initial products may then recombine to regenerate the original polysulphane or disproportionate to give a mixture of polysulphanes containing higher and lower sulphur atoms per chain length:

7

Compound	Bond Dissociation Energy kJ/mole	Reference
HS-SH	$276 \pm 2^{a}$	22
CH ₃ S-SCH ₃	293 ± 2 ^b	18
$C_6H_5S-SC_6H_5$	$230 \pm 1.5^{b}$	28
CH ₃ S-SSCH ₃	$192 \pm 2^{b}$	26
CH ₃ SS-SSCH ₃	$151 \pm 4^{b}$	20
HSS-SSH	146 ± 2 ^a	22
$S_8(ring) \rightleftharpoons \cdot S-S_6$	$-5 \cdot 148 \pm 4^{b}$	27

Table 1.2 Bond Dissociation Energies of S-S Bonds

Estimated from *ab initio* MO calculations. Determined from experimental methods. a

b

$$Ph_2S_4 \longrightarrow 2 PhS_2^{\bullet}$$
 (6)

$$Ph_2S_4 + PhS_2^{\bullet} \longrightarrow Ph_2S_3 + PhS_3^{\bullet}$$
 (7)

 $Ph_2S_4 + PhS_2^{\bullet} \longrightarrow Ph_2S_5 + PhS^{\bullet}$  (8)

etc.

In the presence of an olefin, the disproportionation reaction was suppressed by reaction of sulphur radicals with olefinic bonds:



The thermal instability of dimethyl polysulphanes during analysis using gas chromatography (GC) has been reported. Wajon and co-workers attempted the quantitative determination of dimethyl polysulphanes,  $Me_2S_x$  (x = 2 - 4), using capillary GC [7]. However, it was found that whenever the column temperature exceeded 115°C the dimethyl tetra- and pentasulphanes underwent disproportionation to increase the amount of the lower homologue [7]. This observation again illustrates the weakness of the S-S bonds in organic polysulphanes [6].

Tobolsky and co-workers have investigated the thermal disproportionation of some organic polysulphanes using NMR spectroscopy at 80°C [6,29-30]. Dimethyl tetrasulphane disproportionated rapidly into a mixture of dimethyl di-, tri-, tetra-, penta-, and hexasulphanes when heated at 80°C for 40 hours. The decomposition of dimethyl trisulphane under the same conditions gave only dimethyl di-, tri-, and tetrasulphanes at a much slower rate, a reflection of the greater stability of the S-S bonds in the trisulphane linkage as compared to the S-S bonds in the tetrasulphane linkage. The addition of a stable free radical,  $\beta$ -(phenylnitrogen oxide)- $\beta$ -methylpentane- $\delta$ -one oxide (Banfield's

(13)

free radical) to dimethyl tetrasulphane was found to inhibit the formation of tri-, and higher polysulphanes. A free radical mechanism was suggested to account for the disproportionation products [30]:

	Initiation		
MeS ₄ Me	<u> </u>	2MeS ₂ •	(11)

#### Propagation

 $MeS_4Me + MeS_2^{\bullet}$  $MeS_3Me + MeS_3^{\bullet}$ (12)

$$MeS_4Me + MeS_3^{\bullet} \longrightarrow MeS_5Me + MeS_2^{\bullet}$$
(13)  
$$MeS_5Me + MeS_3^{\bullet} \longrightarrow MeS_6Me + MeS_2^{\bullet}$$
(14)

etc.

Termination

 $MeS_2^{\bullet} + MeS_3^{\bullet}$  $\longrightarrow$ MeS₅Me (15)etc.

#### Figure 1.3 **Disproportionation of Polysulphanes**

However, evidence in support of a free radical mechanism for the decomposition of dimethyl trisulphane was not as conclusive as was found for the decomposition of dimethyl tetrasulphane as the rates of decoloration of Banfield's free radical under the same conditions were slow and of the same order of magnitude as that obtained when the free radical was heated in the absence of trisulphane. If the decomposition of the trisulphane involved free radicals, their rates of formation must be much slower than that observed in the decomposition of the tetrasulphane [29].

Much less information is available on the decomposition of organic polysulphanes to different types of compounds and most studies have been carried out at high temperatures (>200°C). Bock and coworkers investigated the decomposition of a number of dialkyl disulphanes [32]. High temperature pyrolysis of dimethyldisulphane

(>700°C) gave thioformaldehyde, hydrogen sulphide, carbon disulphide, and methane as major products. At lower temperatures, the formation of methanethiol, thioformaldehyde and methane was favoured [32]:

$$CH_{3}-S-S-CH_{3} \longrightarrow CH_{3}SH + CH_{4} + H_{2}C \Longrightarrow S$$
(16)  
$$H_{2}C \Longrightarrow S + H_{2}S + CS_{2} + CH_{4}$$
(17)

Studies by Coope and Bryce on the thermal decomposition of dimethyl disulphane at 316°C indicated that methanethiol, hydrogen sulphide, elemental sulphur and polymeric thioformaldehyde were the major products [33]. The addition of hydrogen sulphide to the dimethyl disulphane in the reaction vessel was found to catalyze the decomposition. This was explained on the basis of production of sulphur in the following manner:

$$H_2S + CH_3SSCH_3 \longrightarrow 1/8S_8 + 2CH_3SH$$
(18)

A free radical mechanism involving the homolytic cleavage of S-S bonds in the disulphane was proposed to account for the various products formed:

$$CH_3SSCH_3 \xrightarrow{316^{\circ}C} 2 CH_3S^{\bullet}$$
(19)

$$CH_3S^{\bullet} + CH_3SSCH_3 \longrightarrow CH_3SH + CH_3SSCH_2^{\bullet}$$
(20)

$$CH_3SSCH_2^{\bullet} \longrightarrow CH_2 \Longrightarrow S + CH_3S^{\bullet}$$
(21)

$$n \operatorname{CH}_2 \Longrightarrow S \longrightarrow (\operatorname{CH}_2 S)_n$$
 (22)

Farmer and Shipley [34], in their extensive study of sulphur-olefin reaction found that all di- and polysulphanes formed from the olefin-sulphur reaction underwent progressive decomposition into hydrogen sulphide, thiol and monosulphide. It is generally believed that cleavage of the S-S bonds in a disulphane or polysulphane leads to the formation of thiols and disproportionation products [34].

#### 1.4 Analysis of Polysulphanes

One of the major problems which hindered early systematic studies of the thermal decomposition of organic polysulphanes was the lack of suitable analytical methods to determine the concentrations of either the reactant polysulphanes or products formed during their decomposition. In many cases, the products are either very volatile (CH₃SH) or thermally unstable (CH₂= S).

Nuclear Magnetic Resonance (NMR) spectroscopy has been demonstrated to be a useful tool for carrying out a qualitative and quantitative analysis of individual polysulphanes in complex mixtures [35-38]. By using simple alkyl end groups, to ensure that there is no complex splitting in the spectra and then carrying out a careful analysis of the proton NMR spectra, it was found that the ¹H chemical shifts for organic polysulphanes vary with the length of the sulphur chain, reaching a constant value for the For dimethyl polysulphanes [36-37], all members up to the long chains [36]. hexasulphane could be separately identified in the mixture. In proton NMR, the integrated area under a given peak is proportional to the number of protons thus making it possible to estimate CH₂/S ratio for a given system. With this ratio the composition of a polysulphane mixture can be quantitatively determined. This method has been used by Tobolsky and co-workers to study the thermal disproportionation of dimethyl polysulphane [30]. Clark and co-workers have also studied the formation of polysulphanes using ¹³C NMR spectroscopy [39]. Polysulphanes up to the octasulphane were identified as shown in Figure 1.4.

High performance liquid chromatography (HPLC), using bonded alkane (reversed) phases appears to be the only current analytical technique for separating organic polysulphanes containing more than 8 sulphur atoms (Figure 1.5) [39-40].



Figure 1.4 ¹³C NMR Spectrum of Bis(4-methylphenyl) Polysulphanes Clark *et al* [39]



Figure 1.5 HPLC Chromatogram (reverse phase, MeOH-H₂O) of Diethyl-Polysulphane (UV detector at 254 nm) [39]

However, with this technique, it is still possible that decomposition of the polysulphanes may occur during analysis especially if the polar stationary phases (silica gel or alumina) come into contact with the polysulphanes. GC separation is difficult if not impossible as the polysulphanes thermally decompose on the column before they are detected and separated, thus giving unreliable results [7].

#### 1.5 <u>Thesis Objective</u>

The use of organic disulphane solvents, particularly dimethyl disulphane and diaryl disulphane in batches or, less commonly, in continuous circulation mode to dissolve deposited sulphur from sour gas production facilities is well established. Organic polysulphanes are the product of sulphur uptake by the disulphane solvents. In these applications, the product polysulphanes may have considerable residence time in the wellstring where the temperatures are relatively high (50° - 150°C). Because of their instability and the formation of radicals, the polysulphanes may decompose under downhole conditions before they can be recovered at the wellhead.

The principal objective of this research was to examine the stability of these polysulphanes under the anticipated downhole conditions. In this study, effort was made to provide some mechanistic interpretation of the observed decomposition products. This required carrying out kinetic studies to establish the rates of the decomposition. Rate studies are often of little value if all the products of the reaction are not fully established. To this end both intermediate and end product analyses were carried out.

Presently, organic disulphane solvents are being used for batch treatments. However, as industry begins to produce the more sour gas wells, large volumes of these solvents will be required and it is envisaged that continuous circulation of the solvent through the wellstring will be needed to economically develop these wells. Because of the high cost of these solvents it therefore becomes necessary to regenerate the spent solvents from the product polysulphanes. This study also aims to provide some information on the possibility of regenerating the disulphane solvents via thermal decomposition of the polysulphanes.

The results of this study should be of value to the sour gas industry because the kinetic information will assist in the process design for a continuous circulation system of the disulphane solvent. Since a study of this nature has not been reported in the literature, it is anticipated that the findings will deepen the present understanding of organic polysulphane chemistry.

Specific objectives of the study were:

- 1. To determine the products of decomposition of  $CH_3S_xCH_3$  and  $ArS_xAr$  in the temperature range 50° 150°C.
- 2. Establish the rate of formation of decomposition products in the presence and absence of  $H_2S$  at 50° 150°C.
- 3. Determine the effect of sulphur loading, that is the value of x in  $RS_xR$ , on the decomposition reactions.
- 4. Examine the influence of decomposition pathways on the conversion of organic polysulphanes to disulphanes or other materials.

#### CHAPTER TWO

#### EXPERIMENTAL METHODOLOGY

#### 2.1 Materials

Chemicals were obtained from commercial suppliers as indicated below and, in general had purities of 99.9% or better. They were used in the study without further purification. Diaryl disulphanes are not available commercially and were prepared using methods described in the literature [42-44].

Dimethyl disulphane, o-, m-, and p-methylthiophenol were obtained from Aldrich Chemical Company Limited; N,N-dimethyl formamide, dimethyl sulphoxide, tetrahydrofuran, sodium thiosulphate, soluble starch and potassium iodate were obtained from Fisher Scientific; potassium iodide, carbon disulphide, and boric acid from BDH Chemicals; recrystallized iodine was obtained from MCB reagents; hydrogen sulphide, nitrogen and cadmium sulphate were obtained from Matheson Gas Products Canada, Inc.

#### 2.2 Preparations

#### 2.2.1 N,N-Dimethyl Formamide Hydrosulphide Catalyst

The hydrosulphide catalyst was prepared by the method described by Clark and his co-workers [39]. Sodium hydroxide (2.10 g, 0.053 mol.) was stirred in dimethyl formamide (97 g, 1.33 mol.) with hydrogen sulphide gas slowly bubbled through the mixture until all the sodium hydroxide had dissolved (5h). The solution gradually turned deep greenish blue as the hydroxide was being taken up. The solution was stored in amber bottle under argon.

# 2.2.2 Dimethyl Polysulphanes (100 wt% Sulphur Loading, average formula CH₃S₅CH₃)

Dimethyl disulphane (100 g, 1.06 mol.) and the hydrosulphide catalyst (0.75 g, 3 wt% in DMF) were weighed into a 500 mL Erlenmeyer flask. Elemental sulphur (100 g, 0.39 mol.) was added and the mixture was stirred at room temperature for 45 minutes or until all of the sulphur had dissolved. HPLC as well as ¹H and ¹³C NMR spectroscopy were then used to determine the composition of the dimethyl polysulphanes. These procedures are described later (p. 27). The ¹H NMR resonances appeared at  $\delta$  ppm 2.40 (CH₃S₂CH₃), 2.55 (CH₃S₃CH₃), 2.63 (CH₃S₄CH₃), 2.66 (CH₃S₅CH₃), and 2.69 (CH₃S₆CH₃). This is in agreement with the chemical shift data reported in the literature [41]. The larger polysulphanes (heptasulphane and larger), though formed, were not identified in the ¹H NMR because the chemical shift difference for the methyl protons in the larger polysulphanes was small and the signal converged at 2.69 ppm (the resonance for hexasulphane) [36,41]. HPLC analysis gave peaks at the retention times (min): 2.84 (Me₂S₂), 4.93 (Me₂S₃), 7.83 (Me₂S₄), 12.25 (Me₂S₅), 16.76 (Me₂S₆), 20.97 (Me₂S₇), 24.54 (Me₂S₈), 25.99 (S₈), 27.63 (Me₂S₉), 30.31 (Me₂S₁₀), 32.61 (Me₂S₁₁), and 34.63 (Me₂S₁₂) (Figure 3.2).

This same preparative method was used to prepare 50 and 200 wt% sulphur-loaded dimethyl polysulphanes.

#### 2.2.3 Diaryl Disulphanes

Diaryl disulphanes were prepared by the method of Fristad and Peterson [42].

*Bis*(2-methylphenyl) disulphane: 2-methylthiophenol (15 g, 0.12 mole) and dimethyl sulphoxide (4.72 g, 0.06 mole) were added to a three-necked flask (250 ml)

and were stirred for twenty-four hours at room temperature. The low-boiling dimethyl sulphane formed was removed under reduced pressure (rotary evaporator). The unreacted thiophenol was removed by dissolving the resulting solution in benzene (50 ml) and then by washing with saturated sodium hydroxide solution. The organic layer was dried (MgSO₄) and benzene was removed by rotary evaporation. Cooling (0°C, 1h) and filtering the solution yielded a whitish crystal mass which was recrystallized from ethanol (150 ml) giving 12.56 g (84%) of the product, m.p.  $35^{\circ}$  -  $36^{\circ}$ C (Lit. m.p.  $38^{\circ}$ C [43]).

*Bis*(3-methylphenyl) disulphane: 3-methyl thiophenol (22.36 g, 0.18 mole) and dimethyl sulphoxide (7.05 g, 0.09 mole) were stirred together in a three-necked flask for 1h. The resulting solution was dissolved in benzene (50 ml) and washed with saturated sodium hydroxide solution. Evaporation of the dried (MgSO₄) organic phase and vacuum distillation of the resulting residue gave 19 g (86%) of the product as a yellow viscous oil, b.p. 144° - 145°C at 33.33 Pa (Lit. b.p. 120°C at 9.33 Pa [42]).

*Bis*(4-methylphenyl) disulphane: 4-methyl thiophenol (15 g, 0.12 mole) and dimethyl sulphoxide (4.72 g, 0.06 mole) were stirred together in a three necked flask for 1h after which the mixture was dissolved in benzene solution (50 ml). The organic phase was washed with sodium hydroxide solution, dried (MgSO₄), concentrated and cooled to 0°C to give white crystals which were recrystallized from ethanol giving 13.63 g (92%) of the product, m.p.  $43^{\circ} - 45^{\circ}$ C (Lit.  $44^{\circ} - 47^{\circ}$ C [44]).

#### 2.2.4 <u>Diaryl Polysulphanes (100 wt%, average formula, ArS, Ar)</u>

Diaryl polysulphane was prepared by placing the aryl disulphane (20 g, 0.08 mole) and the hydrosulphide catalyst (0.75 g) in a 125 ml flask. This was placed in a water bath at 80°C. Elemental sulphur (20 g, 0.08 mole) was added to the disulphane-catalyst mixture after 5 minutes and the mixture was stirred for 24h. At this

temperature, all the sulphur was dissolved by the disulphane. Results of HPLC, ¹H and ¹³C NMR analysis are given in Chapter 3.

#### 2.3 <u>Thermal Decomposition Studies</u>

Two different types of thermal decomposition studies were carried out:

- 1. Experiments in an open system which allowed gaseous products to escape from the reaction vessel as soon as they were formed. These conditions may approximate those found during the batchwise use of solvents in the wellstring or in surface equipment taken "off-line".
- Experiments in an autoclave (closed system) such that the product gases were kept in contact with the reactants. These conditions may approximate those found when solvents are used in systems containing flowing gas.
   These closed system experiments were done in the presence and absence of

hydrogen sulphide/methane mixtures of various compositions. Schematics of the apparatus are shown in Figures 2.1, 2.2 and 2.3.

# 2.3.1 <u>Thermal Decomposition of Dimethyl Polysulphanes -</u> <u>Product Identification</u>

To identify the decomposition products a three-necked round-bottomed flask (250 ml) fitted with a thermometer, magnetic stirrer, condenser and apparatus for withdrawal of gas samples (Figure 2.1) was charged with a known amount of freshly prepared 100 weight % loaded dimethyl polysulphanes (average molecular formula,  $CH_3S_5CH_3$ ). The outlet of the condenser was connected to potassium hydroxide scrubbers to trap any toxic gaseous products. The flask was then flushed with argon to



Figure 2.1 Apparatus for Thermal Decomposition Studies in the Open System

exclude air after which it was heated at 150°C (controlled within ±0.05°C) in a constant temperature oil bath for 24h. Gas samples were withdrawn at specific intervals (2, 7, 12 and 24h) for analysis using gas chromatographic-mass spectrometric (GC-MS) instrumentation. Details of this analysis are given later. GC-MS results indicated the presence of the following gases: methanethiol (m/e 48), carbon disulphide (m/e 76) as major products, thioformaldehyde (m/e 46), methanedithiol (m/e 80) and hydrogen sulphide (m/e 34). When the experiment was concluded, the residue was analyzed by HPLC and ¹³C NMR spectroscopic methods which also gave evidence for the presence of carbon disulphide (retention time = 3.75 min,  $\delta$  = 192.4 ppm) and dimethyl polysulphanes with varying number of sulphur atoms per chain. Detailed results will be given in the next chapter.

#### 2.3.2 Quantification of Decomposition Products: Rate Studies

The preceding experiment showed that methanethiol was one of the major products of decomposition. Its rate of formation was determined in the temperature range of 50°, 75°, 100°, 125° and 150°C in the following manner. A known weight of 100% loaded dimethyl polysulphane (average molecular formula =  $CH_3S_5CH_3$ ) was placed in a three-necked flask connected in series to a condenser and four traps containing 0.05 M iodine solutions. The flask was maintained at the desired temperature and at given time (1, 2 or 24h) intervals the iodine traps were replaced with fresh ones. The amount of iodine consumed in the traps was determined by back titrating the excess iodine with freshly standardized 0.1 M sodium thiosulphate solution and was related to the amount of methanethiol liberated. The chemical reactions involved in determining methanethiol production are as follows:



It is important to note that the H₂S produced reacts with iodine in a similar manner:

 $H_2S + I_2 \longrightarrow 1/8S_8 + 2HI$ 

2.3.3 The Effect of Sulphur Loading on Rates of Formation of Methanethiol

This study was carried out using the method described (above) for the decomposition of 100 wt% loaded dimethyl polysulphane. Known weights of 50 (average molecular formula =  $CH_3S_3CH_3$ ) and 200 wt% (average molecular formula =  $CH_3S_8CH_3$ ) loaded dimethyl polysulphanes were used respectively and the amount of methanethiol liberated was determined from iodometric titration as previously described.

# 2.3.4 <u>Thermal Decomposition of Dimethyl Polysulphane in a Closed System</u> (in the Absence of H₂S)

Although attempts were made to determine the amount of  $CS_2$  produced in the open system experiments, very erratic results were obtained, most likely because of loss of the volatile  $CS_2$ . Consequently, closed system experiments were conducted to make a better determination of the  $CS_2$  produced.

Thermal decomposition of dimethyl polysulphane was studied in a closed system by heating the polysulphanes in a high pressure vessel constructed of Hastelloy C-276 utilizing a titanium alloy seal ring and thrust bolt sealing assembly (Figure 2.2). The vessel was equipped with a BLH model 4310A digital pressure read-out and Fluke Model 2168A digital thermometer-thermocouple arrangement for measuring both the pressure and temperature within the vessel. The system was heated to the desired temperature ( $\pm 1^{\circ}$ C) by an oven with an electrical thermostat control device.




In a typical experiment, a known amount of the polysulphane was weighed and transferred into the vessel. The vessel was sealed and pressure tested to ~13.80 MPa. The vessel was then heated to the desired temperature (90°, 150°, 200°, 250°, 300° and 350°C) for 3 or 48h. Since carbon disulphide was expected to be a major product, at the end of the experiment the vessel was cooled to 6°C to keep the  $CS_2$  in the liquid state while the  $H_2S$  and other gases were released and preferentially absorbed in a series of traps containing 2% cadmium sulphate solution buffered with 4% boric acid [45] and iodine traps (0.05M). The weight of cadmium sulphide precipitated in each trap was determined gravimetrically. Gas analysis by GC showed only trace amounts of methanethiol which could not be quantified by iodometry. The residue in the vessel was weighed and kept for HPLC and NMR investigations (see Chapter 3 for results).

# 2.3.5 Reactions of Dimethyl- and Diaryl Polysulphanes in the Presence of $H_2S/CH_4$ Gas Mixtures

A known amount of the polysulphane was weighed into a glass container connected to an H₂S condenser system as shown in Figure 2.4. Acetone/dry ice slurry (-78°C) was placed in a container which housed the glass tube containing the polysulphane sample as indicated (Figure 2.4) before H₂S was allowed to flow into it. H₂S was liquefied and collected in the container. After a sufficient amount of H₂S was condensed, the container was reweighed to ascertain the exact amount of H₂S charged before placing it in the reaction vessel. The vessel was then sealed and connected to a high temperature/pressure line (Figure 2.3). The composition of hydrogen sulphide was varied with methane and nitrogen. For example 10% H₂S - 90% CH₄, 50% H₂S - 50% CH₄, 100% H₂S and 100% CH₄ were used in one set of the experiments. In each case, the weight of H₂S required to give the desired percentage was condensed into the reaction vessel while the percent of the other gaseous components (from pressure









measurement) was pumped into the vessel through the pressure lines after the vessel had been sealed. The vessel was heated to the desired temperature (90° or 150°C) with continuous stirring for 48 hours. At the end of the experiment the vessel was cooled to  $-10^{\circ}$ C using dry ice before slowly releasing all the H₂S into a KOH scrubber. The residue in the vessel was reweighed and kept for further analysis (NMR, HPLC).

## 2.3.6 <u>Thermal Decomposition of Diaryl Polysulphanes</u>

Bis o-,m-, or p-methylphenyl disulphane (3.5 g, 0.014 mole) was placed in a 125 mL three-necked rounded bottomed flask fitted with a thermometer, condenser, and a magnetic stirrer. The system was heated at 80°C and the hydrosulphide catalyst (0.75 g) was added. After about 3 minutes, elemental sulphur (3.5 g, 0.014 mole) was added to the catalyst-disulphane mixture, which gave 100 wt% loaded diaryl polysulphane. The temperature was raised to 150°C. The experiment was left on for 15 days during which aliquots were taken for HPLC and NMR analysis at 24h intervals. The results of these analyses are given in Chapter 3. The same experiments were repeated at 200°C. No gas production was evident in any of these experiments.

#### 2.4 Analytical Procedures

#### 2.4.1 Nuclear Magnetic Resonance Analysis

Proton (¹H NMR) and carbon (¹³C NMR) nuclear magnetic resonance spectra of reaction products and residues were obtained in CDCl₃ solution on a Bruker AC-200 spectrometer. Residual chloroform resonances ( $\delta = 7.27$  ppm for ¹H, 77.00 ppm for ¹³C) were used as internal reference for spectra measured in CDCl₃.

## 2.4.2 <u>High Performance Liquid Chromatographic (HPLC) Analysis</u>

## HPLC Apparatus and Conditions

All analyses were run on a Model Varian 5000 LC HPLC system equipped with a Valco 10  $\mu$ L injector, a Varian UV-50 detector operating at 230 or 254 nm and a Varian 401 processor. A Waters Nova-Pac octadecylsilyl column (4.6 mm x 15 cm) was used and the column was maintained at ambient temperature. The analysis utilized an isocratic gradient solvent system created by mixing two mobile phases: methanol (A) and water (B). For dimethyl polysulphane, the gradient consisted of linear segments, A : B = 64 : 36 to 100 : 0 over 30 min; for diaryl polysulphane, the gradient was A : B = 80 : 20 to 100 : 0 over 65 min. The flow rate was 1.0 mL/min.

## Sample Preparation and Analysis

Stock solutions of the polysulphane samples (20 mg/mL) were prepared in dry redistilled tetrahydrofuran (THF). After equilibration of the column with the solvent, 10  $\mu$ L of the sample was injected and eluted using the solvent program described above. Peak-area ratios were used to determine calibration factors for carbon disulphide and dimethyl disulphane. Although organic polysulphanes could be detected using this analysis, quantification of these compounds was not possible because of uncertainties in determining calibration factors.

## 2.4.3 Gas Chromatographic-Mass Spectrometry (GC-MS) Analysis

GC-MS analyses were carried out on a Hewlett Packard Model 5870GC/5970B MSD instrument using a supelco SPB-5 30 m x 0.25 mm I.D. column. Helium was used as the carrier gas at a flow rate of 25 mL/sec. The ion source conditions were: temperature 200°C, electron energy 70eV. The GC-MS instrument was operated in total ion monitoring mode.

17.2

## CHAPTER THREE

#### **RESULTS AND DISCUSSION**

## 3.1 Thermal Decomposition in The Open System

## 3.1.1 Determination of Products Formed During the Decomposition of DMPS

The results presented in this section are for the decomposition of a mixture of dimethyl polysulphanes (DMPS) in an open system which allowed gaseous products to escape from the reaction vessel as soon as they were formed so that they could be quantified. The essential aim of the open system experiment was to qualitatively and quantitatively determine the decomposition products of DMPS with a view to obtaining some kinetic information.

The NMR spectra of dimethyl polysulphane (CH₃S_XCH₃) mixtures used in this work are shown in Figure 3.1. Both ¹H and ¹³C NMR spectra show five (5) peaks with a convergence at 2.70 ppm (for ¹H) and 23.50 ppm (for ¹³C) which agreed with those reported in the literature [41]. The HPLC chromatogram (Figure 3.2) shows that the mixture is more complex than revealed by the NMR studies. This implies that dimethyl polysulphane (100 wt% loaded, with x having a number average value of 5) consists of polysulphanes with x in the range of 2 to 12.

When DMPS was thermally decomposed at temperatures in the range of 50° to 150°C, analysis of the produced gases by GC-MS revealed methanethiol and carbon disulphide as the major products of the reaction:

Scheme 1

$$CH_{3}S_{x}CH_{3} \xrightarrow{150^{\circ}C} CH_{3}SH + CS_{2} + H_{2}S + HSCH_{2}SH$$

$$(or CH_{3}SSH)$$

$$Major products Minor products$$



Figure 3.1 NMR Spectra of 100 wt% Sulphur Loaded Dimethyl Polysulphane



Retention Time (min)

Figure 3.2 HPLC Chromatogram of Dimethyl Polysulphane

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Trace amounts of  $H_2S$  were observed along with small quantities of methanedithiol (HSCH₂SH). Selective trapping to remove the  $H_2S$  was carried out by placing 2% solutions of cadmium sulphate buffered with boric acid ahead of the iodine traps. The amount of  $H_2S$  produced, as determined gravimetrically from the precipitated cadmium sulphide, was 0.16g (0.005 mole) and this represents 6% of the total yield of methanethiol (0.082 mole), hence it was a minor product. Similarly, considerable effort was made to condense HSCH₂SH in liquid nitrogen. No material was isolated, hence it may be said to be present only in trace amounts (as indicated by GC-MS analysis). ¹H, ¹³C NMR and HPLC analysis of the residue revealed the presence of CS₂ and unreacted polysulphanes. A mechanistic pathway leading to the above decomposition products will be given later in the section on mechanistic interpretation.

#### 3.1.2 Rate Constant Measurement for the Formation of Methanethiol

Having established that methanethiol and carbon disulphide were the principal products from the thermal decomposition of DMPS, a series of experiments were carried out to determine their rate of formation. Methanethiol, which is a gas at room temperature, is readily quantified by oxidizing it to the disulphane with iodine [46,47]. Carbon disulphide, on the other hand, is a liquid at room temperature. Its extreme volatility and lack of selective trapping reagents for  $CS_2$  in the presence of other components of the system made it more difficult to accurately determine its yield in the open system reaction. As a result carbon disulphide was determined independently as will be discussed in a later section.

In a series of experiments conducted at different temperatures, the liberated methanethiol was determined quantitatively using the iodine titration method [46,47] according to the equation:

$$2 \operatorname{CH}_3 \operatorname{SH} + \operatorname{I}_2 \longrightarrow \operatorname{CH}_3 \operatorname{SSCH}_3 + 2 \operatorname{HI}$$
(1)

Excess iodine was back titrated with standard sodium thiosulphate solution (0.10 M) using starch as an indicator:

$$2 S_2 O_3^{2-} + I_2 \longrightarrow S_4 O_6^{2-} + 2 I^-$$
 (2)

Although the iodometric titration method gives abnormal results with higher and tertiary aliphatic thiols [48,49], reactions of methanethiol, ethanethiol and thiophenol with iodine are rapid and complete [50,51] hence this method was adequate for this work. The accuracy of methanethiol determination can be limited by the presence of hydrogen sulphide which also reacts quantitatively with iodine. Therefore the results presented here for methanethiol actually includes the  $H_2S$  (~6% of total methanethiol) produced during the decomposition.

Tables 3.1 through 3.4 show the results obtained from the decomposition of 50  $CH_3S_3CH_3$ ), 100 ( $CH_3S_5CH_3$ ) and 200 ( $CH_3S_8CH_3$ ) weight % sulphur loaded DMPS solutions at 50°, 75°, 100°, 125° and 150°C. The replicate values at each temperature are given in brackets. These data represent the concentration of methanethiol (6% of  $H_2S$  inclusive) as a function of time as determined by direct chemical analysis. For kinetic data to be informative or interpreted in terms of reaction mechanisms, rate expressions are required. Although the thermal decomposition of DMPS is by no means a simple process, all the data accumulated for the formation of methanethiol were first tested with simple first-order and second-order kinetic rate expressions.

### 3.1.3 Test for Reaction Order with Respect to Methanethiol Formation

Data were tested using the standard integrated expressions for first (equation 3.1) and second order (equation 3.2) reactions:

	CH ₃ SH Concentrations (moles x 10 ⁻³ ) at ^b				
Time (h)	· 50°C	75⁰C	100°C		
24	0.365 (0.365)ª	1.100 (1.133)	0.840 (0.812)		
48	0.623 (0.679)	2.036 (2.084)	1.940 (1.860)		
72	0.924 (0.992)	3.040 (2.989)	3.280 (3.090)		
96	1.203 (1.265)	3.997 (3.919)	4.460 (4.346)		
120	1.525 (1.640)	4.754 (4.646)	5.500 (5.348)		
144	1.740 (1.914)	5.423 (5.292)	-		
168	2.165 (2.207)	-	-		
192	2.423 (2.501)	-	-		

## Table 3.1 Production of $CH_3SH$ from DMPS at Different Temperatures

a

Values of replicate experiments are given in parentheses. Initial moles of DMPS were 0.1318, 0.1063 and 0.0851 at 50°, 75° and 100°C. b

.

	CH ₃ SH Concentrations (moles x $10^{-3}$ ) at ^b		
Time (h)	125°C	150°C	
. 1	0.80 (0.95)ª	4.80 (4.80)	
2	1.00 (1.20)	10.50 (10.80)	
4	1.30 (1.50)	14.60 (15.40)	
6	1.40 (1.70)	21.50 (22.10)	
8	2.60 (2.50)	-	
10	5.30 (5.00)	-	
12		43.20 (41.50)	
24	14.00 (14.10)	81.00 (81.80)	
48	19.60 (19.70)	152.00 (150.00)	

Production of CH₃SH from DMPS at Different Temperatures

a b Values of replicate experiments are given in parentheses. Initial moles of DMPS was 0.266 for both temperatures.

## Effect of Sulphur Loading on $CH_3SH$ Production at 75°C

	$CH_3SH$ Concentrations (moles x 10 ⁻³ ) at ^b				
Time (h)	50 wt% S ₈ Loading	100 wt% S ₈ Loading	200 wt % S ₈ Loading		
24	0.760 (0.768) ^a	1.200 (1.133)	0.874 (0.893)		
48	1.403 (1.400)	2.084 (2.036)	1.644 (1.762)		
72	2.132 (2.082)	2.989 (3.040)	2.745 (2.655)		
96	2.759 (2.802)	3.919 (3.997)	3.082 (3.034)		
120	3.448 (3.421)	4.646 (4.754)	3.267 (3.266)		
144	4.009 (4.048)	5.292 (5.423)	-		

a

Values of replicate experiments are given in parentheses. Initial moles of DMPS were 0.1489, 0.1063 and 0.1595 for 50, 100 and ь 200 weight % loadings.

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	$CH_3SH$ Concentrations (moles x 10 ⁻³ ) at ^b				
Time (h)	50 wt% S ₈ Loading	100 wt% S ₈ Loading	200 wt% S ₈ Loading		
1	0.018 (0.019)ª	4.800 (4.800)	0.392 (0.384)		
2	-	10.500 (10.800)	-		
3	0.102 (0.198)	-	6.584 (5.920)		
4	-	14.600 (15.400)	-		
5	0.369 (0.374)	-	13.976 (13.360)		
6	-	21.500 (22.100)	-		
7	0.669 (0.648)	-	-		
8	-	-	22.497 (21.782)		
11	1.078 (1.059)	-	29.953 (29.256)		
12	<b>-</b> '	42.000 (41.500)	<del>.</del>		
14	-	-	35.569 (34.684)		
24	1.568 (1.513)	81.000 (81.800)	44.353 (43.716)		
48	2.083 (2.111)	152.000 (150.000)	-		

# Effect of Sulphur Loading on $CH_3SH$ Production at 150°C

a

Values of replicate experiments are given in parentheses. Initial moles of DMPS were 0.1489, 0.1063 and 0.1595 for 50, 100 and b 200 weight % loadings.

First Order:

$$\ln[A]_{t} = \ln[A]_{0} - k_{1}t \tag{3.1}$$

Second Order:

$$\frac{1}{[A]_{t}} = \frac{1}{[A]_{0}} + k_{2}t \qquad (3.2)$$

A graphical analysis of the concentration-time data using first order kinetics (equation 3.1) gave a straight line showing that the formation of methanethiol is consistent with first-order kinetics within the limits of experimental error (Figure 3.3). Data obtained at lower temperatures were also consistent with first order kinetics. The rate of formation of methanethiol from the thermal decomposition of dimethyl disulphane has previously been shown to follow a first-order kinetics [52].

Figure 3.4 is a graphical illustration of a second-order plot for the concentration-time data obtained at 150°C. The deviation from linearity implies that second-order kinetics does not apply for the formation of methanethiol from DMPS under these conditions.

First-order rate constants computed from the slope of the straight lines of the plots and the corresponding half-life at each temperature are given in Table 3.5. As can be seen from these data, the rate of production of methanethiol at 150°C is such that half of the initial DMPS is lost to methanethiol in approximately 1.7 days. If the amount of DMPS lost to  $CS_2$  is included, the overall half-life for 100 weight % loaded DMPS (CH₃S₅CH₃) decomposition at 150°C will be less than 1.7 days.

Experience has shown that 150°C is at the top end of temperatures found in sour gas reservoirs in Alberta and thus data at lower temperatures (50° - 100°C) is of particular interest in such a setting. For example, at 75°C, the half-life for the loss of 100 weight % sulphur loaded DMPS ( $CH_3S_5CH_3$ ) to methanethiol is ca. 80 days; if the loss to  $CS_2$  is factored in, a value of approximately 50 days is estimated (based on a mechanistic proposal to be discussed in Section 3.5). This temperature is perhaps typical of the intermediate reservoir to wellhead temperature in many sour gas fields. As a







[		
Temperature (°C)	Rate Constant (Sec ⁻¹ )	Half Life (days)
50	$202.20 \pm 1.73$	$296.6 \pm 1.96$
. 75	745.60 ± 5.18	$80.30 \pm 0.56$
100	$1171.60 \pm 0.43$	$51.11 \pm 0.02$
125	$3552.00 \pm 0.86$	$16.86 \pm 0.003$
150	35,307.00 ± 0.86	$1.65 \pm 0.002$

## Influence of Temperature on the Rate of Methanethiol Production

Table 3.5

Rate constants and half lives given above are average of two values.

result, it appears that dimethyl disulphane (DMDS) could be used in such sour gas systems without large losses.

## 3.1.4 Temperature Dependence of Reaction Rates

The exponential temperature dependence of a reaction rate constant for the formation of methanethiol is illustrated in Figure 3.5. The energy of activation  $E_a$ , for the reaction was computed from Arrhenius equation:

$$k = A e^{-E_a/RT}$$
(3.4)

which, for convenience, is frequently used in the following form:

$$\ln k = \ln A - E_a/RT \tag{3.5}$$

The constant A is called the pre-exponential or frequency factor.

The temperature dependence of the rate of methanethiol formation was determined by using rate constants obtained between 50° and 150°C (Table 3.5). As illustrated in Figure 3.6, an Arrhenius plot gave a reasonably straight line fit with a slope of -2757.1 and an intercept (log A) of 10.77. The energy of activation ( $E_a$ ) and pre-exponential factor (A) for the reaction were calculated as  $52.80 \pm 4.34$  kJmol⁻¹ and  $(5.86 \pm 1.17) \times 10^{10}$ s⁻¹. The temperature dependence of k₁ in the range of 50° - 150°C is given as

$$k_1 = (5.88 \pm 1.17) \times 10^{10} \exp[(-52.80 \pm 4.34 \text{ Jmol}^{-1})/\text{RT}]\text{s}^{-1}$$
 (3.6)

The uncertainties represent 95% confidence limits as obtained from the least squares method.

The low value of  $E_a$  can be explained in terms of the weakness of the S-S bonds in dimethyl polysulphane. Experimental and theoretical values of S-S bond dissociation energies for dimethyl tetrasulphane and hydrogen tetrasulphane are given in Table 1.2. A lower value can be expected for dimethyl pentasulphane which represents the average polysulphane used in this work since the bond dissociation energy for the polysulphanes decreases with increasing chain length [6].



Figure 3.5 Variation of the First Order Rate Constant for the Production of Methanethiol as a Function of Temperature





Kende and co-workers [53] have also measured the temperature dependence of  $k_1$  for the thermal disproportionation of pure dimethyl tetrasulphane in the range 50° - 80°C and estimated  $E_a$  to be 153 kJ which is different from a value of 52.80 kJ determined in this study. It must be emphasized that these are two different reactions. Also a complex mixture of DMPS (CH₃S_XCH₃) with x in the range of 2 to 7 was used instead of pure CH₃S₅CH₃. Although a mixture of polysulphane (CH₃S_XCH₃), with x values in the range of 2 to 7 was used in this work, the overall rate is expected to be higher because of the larger proportion of CH₃S₅CH₃ to the other polysulphanes having x = 3, 4, 6 and 7.

## 3.1.5 Effect of Sulphur Loading on Methanethiol Production

In the preceding section, only data for 100 weight % sulphur loaded DMPS  $(CH_3S_5CH_3)$  with an average of 5 sulphur atoms per polysulphane molecule have been described. It was thought that dimethyl polysulphanes with lower and much higher sulphur loading than 100 weight %  $(CH_3S_5CH_3)$  may influence the rate of  $CH_3SH$  production from DMPS decomposition. The work was therefore extended to 50  $(CH_3S_3CH_3)$  and 200  $(CH_3S_8CH_3)$  weight % sulphur loaded DMPS under similar conditions used for the 100 weight % sulphur loaded DMPS  $(CH_3S_5CH_3)$ .

First-order rate constant results were obtained at 75° and 150°C by using the procedure described above, these data are given in Table 3.6. A plot of rate constant against weight % sulphur loading is depicted in Figure 3.7. The observed trend in the results may be explained in terms of bond dissociation energy. 50 weight % sulphur loading ( $CH_3S_3CH_3$ ) would result in dimethyl polysulphanes with an average of 3 sulphur atoms per molecule while 200 weight % sulphur loading ( $CH_3S_8CH_3$ ) would yield DMPS with 8 sulphur atoms per molecule on the average. Consequently the S-S bond strength would decrease in going from 50 ( $CH_3S_3CH_3$ ) to 200 weight % sulphur loaded DMPS ( $CH_3S_8CH_3$ ) since the higher polysulphanes are more unstable [6]. Thus

% Sulphur Loading (Wt%)	k at 150°C ^a (Sec ⁻¹ )	k at 75°C ^a (Sec ⁻¹ )
50	$642.00 \pm 0.86$	$342.14 \pm 0.26$
100	35,307.00 ± 0.86	$745.60 \pm 5.18$
200	30,758.40 ± 2.60	377.57 ± 0.35

# Table 3.6Effect of Sulphur Loading on Methanethiol Production

^a Rates quoted are average of two values.



Figure 3.7 Effect of Sulphur Loading on Methanethiol Production

the population of methylthio radicals and hence the rate of hydrogen atom abstraction to form CH₃SH could differ significantly.

Lower rates of CH₃SH production from 50 weight % sulphur loaded DMPS  $(CH_3S_3CH_3)$  can be explained on the basis that such solutions contain smaller DMPS (mainly CH₃S₃CH₃) molecules which have stronger S-S bonds, thereby resulting in slower decomposition rates. For the same reason, the rates were expected to be higher for 100 (CH₃S₅CH₃) and 200 weight % sulphur loaded DMPS (CH₃S₈CH₃). However, 200 weight % sulphur loaded DMPS (CH₃S₈CH₃) produced less CH₃SH than the 100 weight % DMPS (CH₃S₅CH₃) solution. A plausible explanation could be that the larger polysulphanes contain less abstractable hydrogen per molecule by virtue of their higher sulphur to carbon and hydrogen ratio. As a result there is a high probability that some of the methanethiol formed could encounter elemental sulphur and be oxidized, according to the equation:

 $2 \text{ CH}_3\text{SH} + \text{S} \longrightarrow \text{CH}_3\text{SSCH}_3 + \text{H}_2\text{S}$ 

# 3.2 <u>Studies on the Thermal Decomposition of Dimethyl Polysulphane in a Closed</u> <u>System</u>

As mentioned in the preceding section, the amount of  $CS_2$  produced could not be measured accurately from the open system experiment because of its high volatility. Experiments were therefore conducted in a closed system so as to keep all the volatile products in the reaction vessel. The principal products from the closed system experiment as revealed by gas chromatographic analysis of the sampled gas were  $CS_2$ and  $H_2S$ . Traces of methanethiol and methane were found in the gas phase. Thus, unlike open system experiments, methanethiol was not a major product. At the termination of the experiment, the reaction vessel was maintained at about  $6^{\circ}C \pm 1^{\circ}C$  to keep as much of the CS₂ as possible in the liquid state during the release of gas from the reaction vessel. The H₂S in the effluent gas was quantified gravimetrically by precipitating it as cadmium sulphide in acidified cadmium sulphate traps. Methanethiol was determined using iodine traps placed after the cadmium sulphate traps. The yield of methanethiol was about 1% of the yield of H₂S. The amount of CS₂ in the liquid residue was determined using HPLC. Methanethiol, a major product in the open system experiment, was only observed as a minor product in the closed system experiment. It is likely that the methanethiol produced underwent a secondary reaction with the polysulphane sulphur to produce dimethyl disulphane (DMDS) and the observed hydrogen sulphide as discussed in a later section (3.5.2).

In Table 3.7, the weight of each major volatile product produced over the reaction time is presented. These results are interesting from an industrial perspective because the closed system experiments may approximate more closely conditions found in wellstring. Unlike the open system experiments, no decomposition was observed at 90°C and the weight of the recovered material was almost 100%. Since 90°C is the typical reservoir temperature for most sour gas wells in Alberta, the result suggests that dimethyl disulphane could reasonably be used in such reservoirs with minimum losses. One note of caution to industrial users is, however, to remember that these experiments were conducted in the absence of H₂S. Data collected at 125° and 150°C indicated that DMPS decomposed to carbon disulphide and hydrogen sulphide with most decomposition occurring at 150°C. These observations indicate that it may not be viable to use dimethyl disulphane to remove sulphur plugs from sour gas facilities in high hydrogen sulphide containing reservoirs because many super sour reservoirs have temperatures in excess of 100°C [17].

## Products from the Decomposition of DMPS in a Closed Reactor System

Temperature (°C) ^a	Initial DMPS (g)	Recovered DMPS (g)	CS ₂ in Recovered DMPS (g)	H ₂ S ^b Produced (g)	% Mass Recovery ^c
90	40.24	40.00	-	-	99.4
•	40.00	39.50	-	-	98.8
125	40.26	36.67	2.42	0.80	93.1
	40.14	37.08	2.48	0.77	94.3
150	40.02	29.30	5.65	1.90	78.0
	39.43	28.84	5.82	1.87	77.9

а

Residence time was 48h. Only traces of methanethiol were observed in these experiments. Efforts to improve these mass balances were unsuccessful. b

с

A rough analysis of the data obtained at  $125^{\circ}$  and  $150^{\circ}$ C indicates that the two major products, CS₂ and H₂S were formed in a 3:1 ratio. This is consistent with the proposed mechanism discussed under section 3.5.

## 3.3 Decomposition of DMPS in a Closed System in the Presence of H₂S

Dimethyl polysulphane, once formed, will have a long residence time in the wellstring where it will be exposed to the hydrogen sulphide of the sour gas. The purpose of this investigation was to determine the influence of hydrogen sulphide composition on carbon disulphide production from the thermal decomposition of dimethyl polysulphane. Mixtures of hydrogen sulphide and methane gases were used since most sour gas wells nearly always contain low molecular weight hydrocarbons. In addition, a mixture of  $H_2S$  and nitrogen was used to observe any additional influence of inert gas used to provide overpressure. It was difficult to quantify the  $H_2S$  produced in these experiments since the hydrogen sulphide added to the reactor would far exceed that formed in the decomposition.

Data obtained at 90° and 150°C are given in Table 3.8. In this study, only carbon disulphide was quantified although it is possible that traces of methanethiol may have been formed as was observed in the closed system experiment carried out in the absence of  $H_2S$ . In these experiments, acceptable mass recoveries were obtained. As was observed in closed system experiment without  $H_2S$  no decomposition occurred below 90°C.

The extent of decomposition of DMPS observed at 100°C for the open system experiments at longer reaction time (180h) (Table 3.1), indicates that minimum decomposition would be observed at 90°C over a reaction time of 48h. Data in Table 3.9 show the effect of gas composition on  $CS_2$  formation from DMPS at 150°C. It is evident from Table 3.9 that the addition of hydrogen sulphide to DMPS does have a significant

Gas Composition (%)	Initial DMPS (g)	Recovered DMPS (g)	CS ₂ in Recovered DMPS (g)	% Mass Recovery
100% H ₂ S	21.39	20.09	0.382	93.9
	22.96	21.34	0.405	95.9
50% H ₂ S - 50% CH ₄	20.43	19.70	0.817	96.4
	20.68	19.72	0.709	95.4
50% H ₂ S - 50% N ₂	21.33	20.58	0.720	96.5
	21.50	20.75	0.732	96.5
10% H ₂ S - 90% CH ₄	20.05	18.84	1.800	94.0
	20.15	19.01	1.850	94.3
10% H ₂ S - 90% N ₂	20.74	19.46	1.712	93.8
	22.19	20.50	1.702	92.4
100% CH ₄	21.12	20.27	1.297	96.0

Production of  $CS_2$  from DMPS in the Presence of  $H_2S$  at 150°C

Та	ble	3.9

Effect of Gas Composition on  $CS_2$  Formation at  $150^{\circ}C^{a}$ 

Gas Composition	Wt% CS ₂ in Recovered DMPS	
No gas over pressure	19.8	
100% H ₂ S	1.9	
50% H ₂ S - 50% CH ₄	3.9	
50% H ₂ S - 50% N ₂	3.5	
10% H ₂ S - 90% CH ₄	9.6	
10% H ₂ S - 90% N ₂	8.5	
100% CH ₄	6.4	

^a Data derived from results shown on Tables 3.7 and 3.8

effect on carbon disulphide production. Decomposition of DMPS to  $CS_2$  was highest when there was no gas over pressure. The amount of  $CS_2$  produced represents 19.8% of the total recovered liquid DMPS. With 100% H₂S over pressure, the amount of  $CS_2$ produced was only 1.9% of the recovered liquid DMPS. These results suggest that the presence of hydrogen sulphide can decrease DMPS conversion to  $CS_2$ . In terms of the industrial application of dimethyl disulphane for sour gas production facilities, the results indicate that little decomposition of the formed DMPS will occur in the wellstring and under downhole conditions. Lesser decomposition of DMPS is anticipated if dimethyl disulphane is used to dissolve the expected sulphur deposit when producing the super sour gas wells.

The  $H_2S$  composition was also varied with nitrogen in place of the methane gas. As can be seen from Tables 3.8 and 3.9, there is no significant difference in the amount of  $CS_2$  formed when compared with the corresponding values obtained for  $H_2S$  -  $CH_4$ compositions. The reaction between the methane gas and sulphur is an important industrial process that has been widely studied [3,54]:

$$CH_4 + 1/2 S_8 \longrightarrow CS_2 + 2 H_2 S$$
 (3.5)

This reaction apparently does not seem to have occurred in this study and if it occurred at all, only to a small extent. The reaction only becomes important at higher temperatures in the range of 800° - 1000°C [3]. A mechanism consistent with these observations has been proposed and will be discussed under a section on mechanistic interpretation.

## 3.4 <u>High Temperature Experiments</u>

One of the objectives of this research was to investigate the stability of DMPS at temperatures between 50° and 150°C. Data obtained at 150°C for the decomposition of DMPS in the closed system indicated that  $CS_2$  and  $H_2S$  were major products. To have

an idea of what will happen at higher temperatures, DMPS was decomposed in a closed reactor for 3h between 200° and 350°C and the data collected are shown in Table 3.10. Decomposition rates were higher and at 350°C, the amount of  $CS_2$  produced over 3h almost doubles that obtained at 150°C at 48h reaction time.

¹³C NMR of the liquid residue collected after a reaction time of 3h is shown in Figure 3.8. As indicated, only dimethyl disulphane and perhaps traces of the trisulphane were left in the residue which suggests that almost all the DMPS was converted to  $CS_2$ and  $H_2S$ . The amount of  $CS_2$  produced within 3h at temperatures in the range of 250° -350°C seems to be fairly constant. It is possible that the decomposition was completed with this reaction time. The mass recoveries in these experiments, however, were poor. The poor material balance is probably due to losses of the highly volatile  $CS_2$  since it is difficult to recover the residue from the autoclave vessel without significant  $CS_2$  losses.

The implication of these findings is that at higher temperatures, thermal decomposition may become an alternative method of disposing of spent dimethyl disulphane by conveniently converting the recovered DMPS to  $CS_2$  and  $H_2S$ . Carbon disulphide is an important organic solvent while the hydrogen sulphide can be converted to elemental sulphur using conventional Claus technology.

## 3.5 Comments on the Chemical Mechanism of DMPS Decomposition

# 3.5.1 <u>Thermal Decomposition of DMPS in an Open System in the Absence of</u> <u>Hydrogen Sulphide</u>

Principal reaction products from the decomposition of dimethyl polysulphane in an open system were methanethiol, carbon disulphide and hydrogen sulphide. The free radical reaction mechanism shown in Figure 3.9 explains the formation of these products. Although there was no direct evidence suggesting the existence of free

Temperature (°C)	Initial DMPS (g)	Recovered DMPS (g)	CS ₂ in Recovered liquid (g)	H ₂ S ^c Produced (g)	% Mass Recovery
200 ^b	40.05	22.80	8.25	2.89	64.1
	40.10	22.80	8.44	2.90	64.1
250	40.42	22.14	11.60	4.23	65.2
	40.30	21.50	11.18	4.20	63.8
300	40.43	21.31	11.87	5.43	66.1
	40.42	20.48	11.35	5.40	64.0
350	40.43	20.84	11.90	4.73	63.2
	40.42	20.75	11.89	4.79	63.2

**Table 3.10** Products from the Decomposition of DMPS in a Closed Reactor System ^a

а

b

Residence time was 3 h Residence time was 48 h Only traces of CH₃SH were observed in these experiments С

57



(a) Proton decoupled ¹³C NMR of DMPS before thermal treatment

(b) Proton decoupled ¹³C NMR of DMPS after thermal treatment



Figure 3.8 ¹³C NMR Spectra of 100 wt% Sulphur Loaded Dimethyl Polysulphane

Initiation  

$$CH_3S_xCH_3 \longrightarrow CH_3S^{\bullet} + CH_3S^{\bullet}_{x-1}$$
 (1)

Propagation

$$CH_3S^{\bullet} + CH_3S_xCH_3 \longrightarrow CH_3SH + CH_3S_xCH_2^{\bullet}$$
(2)

$$\overset{H_{\bullet}}{\searrow} S \underset{S_{x-4}}{\overset{S}{\longrightarrow}} CS_2 + HS_{x-3}^{\bullet}$$
(4)

Termination

$$2CH_3S_{x-1} \bullet CH_3S_{2x-2}CH_3$$
 (5)

$$CH_3S_{x-1}^{\bullet} + CH_3S^{\bullet} \longrightarrow CH_3S_xCH_3$$
 (6)

$$2 CH_3S^{\bullet} \longrightarrow CH_3SSCH_3$$
(7)  
(Less likely)

$$2HS_{x-3} \bullet H_2S_{2x-6} \tag{8}$$

$$H_2S_{2x-6} \longrightarrow H_2S + S_{2x-7}$$
 (9)

$$\overset{\text{H}_{\bullet}}{\underset{S}{\underset{S_{x,4}}{\overset{S}{\longrightarrow}}}} S + CH_3S^{\bullet} \longrightarrow CH_3SH + CS_2 + x-3/8S_8$$
(10)
radicals in this study, other studies on the thermal disproportionation of organic polysulphanes [6] and the thermal decomposition of dimethyl disulphane [33] did confirm their presence even at as low a temperature as 50°C.

The elementary step in the thermal decomposition of DMPS involves the unimolecular homolytic rupture of an S-S bond. If cleavage occurs at the first S-S bond, then methylthio and methylpolythio radicals (Equation 1) would be formed. Cleavage of other S-S bonds would lead to a range of polythio radicals depending on the chain length of the initial polysulphane. One fate of methylthio radicals would be the formation of methanethiol via hydrogen abstraction from the methyl group of DMPS (Equation 2), which initially is the only source of hydrogen atoms. This is consistent with the observed fate of methylthio radicals produced from the thermal decomposition of dimethyl disulphane at 350°C [33].

The new radical,  $CH_3S_xCH_2^{\bullet}$ , that would be produced as a result of the hydrogen abstraction, is proposed to undergo intramolecular transformation to a heterocyclic intermediate with the expulsion of one equivalent of methanethiol (Equation 3). The formation of this cyclic intermediate would depend on the proportion of  $CH_3S_xCH_2^{\bullet}$ having  $x \ge 4$ . Subsequent radical-radical interaction between the cyclic radical intermediate and a methylthio radical would result in the formation of one mole of carbon disulphide and another mole of methanethiol (Equation 4). Based on this mechanistic proposal it might be expected that methanethiol and carbon disulphide would be formed in a 3:1 ratio. For intermediates of the type,  $CH_3S_xCH_2^{\bullet}$ , x < 4, a stepwise mechanism may be more likely:

$$CH_3S_xCH_2^{\bullet} \longrightarrow CH_3S_{x-1}^{\bullet} + {}^{\bullet}CH_2S^{\bullet}$$
(11)

•CH₂S• 
$$\xrightarrow{\text{CH}_3\text{S}^{\bullet}_{x-1}}$$
 •SCH₂S• + CH₃S•_{x-2} (12)

$$SCH_2S^{\bullet} \longrightarrow CS_2$$
 (13)

$$CH_3S^{\bullet}_{x-2} \longrightarrow CH_3SSH$$
 (14)

$$CH_{3}S^{\bullet}_{x-2} \longrightarrow CH_{3}S^{\bullet} + {}^{\bullet}S^{\bullet}_{x-3}$$
(15)

$$^{\circ}S^{\circ}_{x-3} \longrightarrow H_2S$$
 (16)

Several modes of termination of the active radical species can be envisioned (Reactions 5 - 10 in Figure 3.9). Recombination of polythio and/or methylthio radicals would regenerate dimethyl di- or polysulphanes which would be recycled through reactions 1 - 4. Recombination of two methylthio radicals to give dimethyl disulphane (Equation 7) is one example of this type of reaction. Recombination of hydrogen polythio radicals may yield hydrogen polysulphane (Equation 8) which could decompose to give the observed hydrogen sulphide (Equation 9). The reaction stoichiometry could not be verified experimentally because of the difficulties in simultaneously quantifying  $CS_2$  in the presence of  $CH_3SH$  in the open system studies. However, the proposed mechanism is consistent with the experimental findings that methanethiol and carbon disulphide were major products with hydrogen sulphide being formed only in lesser amounts.

Rao *et al* [55] proposed a combination-disproportionation reaction of methylthio radicals represented by Equation 17 to explain the photo-decomposition of dimethyl disulphane but obtained inconclusive results in their attempt to isolate any thioformaldehyde as a possible product:

$$2 \operatorname{CH}_3 S^{\bullet} \longrightarrow H_2 C = S + C H_3 S H$$
(17)

No evidence in support of thioformaldehyde formation was obtained in this study although it is possible that any thioformaldehyde formed was consumed in secondary reactions (e.g. polymerization).

### 3.5.2 Thermal Decomposition of DMPS In a Closed System

Methanethiol which was a major product in the open system experiment was only a minor product in the closed system experiment, while  $CS_2$  and  $H_2S$  were major products (Tables 3.7 and 3.10). A free radical mechanism, similar to that already proposed for the open system decomposition is compatible with the experimentally observed data for the thermal decomposition of DMPS in a closed system excepting that additional reactions are needed to account for the pronounced decrease in methanethiol yield.

Reactions (23) to (26) describe the possible fate of the methanethiol produced in the closed system experiment. Sulphur would readily be formed from the partial decomposition or rearrangement of DMPS [33] as depicted by reaction (22). These reactions shown in Figure 3.10 are likely to be operative in the open system also, though to a much lesser degree since the volatile methanethiol readily escapes the system.

## 3.5.3 Thermal Decomposition of DMPS in The Presence of $H_2S$ , $N_2$ and $CH_4$ Gas Mixtures

The aim of these experiments was to determine the effect of  $H_2S$  on the production of  $CS_2$  from DMPS. It was observed that the yield of  $CS_2$  was significantly reduced in the presence of added  $H_2S$  gas mixed with either methane or nitrogen. To explain the appreciable decrease in  $CS_2$  yield, the following mechanism is proposed:

$$CH_3S_xCH_3 \longrightarrow CH_3S^{\bullet} + CH_3S_{x-1}^{\bullet}$$
 (18)

$$CH_{3}S^{\bullet} + CH_{3}S_{x}CH_{3} \longrightarrow CH_{3}SH + CH_{3}S_{x}CH_{2}^{\bullet}$$
(19)

$$\overset{H_{\bullet}}{\searrow} \overset{S}{\underset{S_{x}}{\overset{S}{\times}}} + CH_{3}S^{\bullet} \longrightarrow CH_{3}SH + CS_{2} + x-3/8S_{8}$$
(21)

### The Fate of Methanethiol

$$CH_3S_xCH_3 \longrightarrow CH_3S_{x-1}CH_3 + 1/8S_8$$
 (22)

$$CH_3SH + 1/8S_8 \longrightarrow CH_3SSH$$
(23)

$$CH_3SSH + CH_3SH \longrightarrow CH_3SSCH_3 + H_2S$$
(24)

$$CH_{3}SH + CH_{3}S_{x}CH_{2}^{\bullet} \longrightarrow CH_{3}S_{x}CH_{3} + CH_{3}S^{\bullet}$$
(25)

$$2CH_3S^{\bullet} \longrightarrow CH_3SSCH_3$$
 (26)

# Figure 3.10 Proposed Mechanism for the Thermal Decomposition of DMPS in the Closed System

$$\dot{CH}_3S_xCH_3 \longrightarrow CH_3S^{\bullet} + CH_3S_x^{\bullet}$$
 (27)

$$CH_3S^{\bullet} + H_2S \longrightarrow CH_3SH + HS^{\bullet}$$
 (28)

$$CH_3S^{\bullet} + CH_3S_xCH_3 \longrightarrow CH_3SH + CH_3S_xCH_2^{\bullet}$$
(29)

$$CH_3S_xCH_2^{\bullet} \longrightarrow CS_2$$
 (30)

$$2CH_3SH + 1/8S_8 \longrightarrow CH_3SSCH_3 + H_2S$$
(31)

$$2HS^{\bullet} \longrightarrow HSSH \longrightarrow 2H_2S + 1/8S_8$$
(32)

The differences between this reaction scheme and that proposed for the closed system experiment without added  $H_2S$  lies in the fate of the methylthio radical produced. In this present scheme, the methylthio radical can abstract hydrogen from hydrogen sulphide (Equation 28) or from the methyl groups of dimethyl polysulphane (Equation 29). If the reaction represented by Equation 28 competes significantly with the reaction represented by Equation 29, a lower yield for  $CS_2$  would be predicted. Also,  $CH_3S_XCH_2^{\bullet}$  could be scavenged by  $H_2S$ , i.e.

$$H_2S + {}^{\bullet}CH_2S_{\chi}CH_3 \longrightarrow CH_3S_{\chi}CH_3 + HS^{\bullet}$$
(33)

As proposed previously the generation of the  $CH_3S_XCH_2^{\bullet}$  radical would ultimately result in  $CS_2$  formation. Dimethyl disulphane formed during the course of these reactions would be recycled to dimethyl polysulphane if it encounters elemental or polysulphane sulphur as shown below:

$$CH_3SSCH_3 + S_x \longrightarrow CH_3SS_xSCH_3$$
 (34)

Reaction (34) is responsible for the success of dimethyl disulphane as a solvent for mitigating the sulphur deposition problem often encountered during the production of sour natural gas reservoirs.

Although the above mechanisms seem reasonable, it is difficult, if not impossible, to prove them absolutely since the proposed intermediates and polysulphanes cannot be isolated or analysed within the complex mixtures which exist in the DMPS system. However, the mechanism proposed involving free radical pathways has some precedent, for example, in the thermal decomposition of dimethyl disulphane [33] and disproportionation of DMPS [29-31]. Because of the nature of the catalyst used in preparing the DMPS used in these studies, it is possible that ionic mechanisms may be operating. However, the general weakness of the S-S bonds in organic polysulphanes and the thermal conditions (up to 150°C) under which this study was carried out seems to favour free radical mechanism as the polysulphane would readily decompose to free radical species.

## 3.6 <u>The Thermal Decomposition of Diaryl Polysulphane in the Absence and in the</u> <u>Presence of Hydrogen Sulphide</u>

Besides the use of dimethyl disulphane for removing sulphur plugs formed in a wellstring producing sour gas, there is a growing interest in the use of diaryl disulphanes for similar purposes since studies have shown that diaryl disulphanes have sufficient sulphur uptake capacity to be useful for mitigating the problem of sulphur deposition in sour gas production facilities [56]. At present, two major gas fields (Obed in Alberta and Labarge in Wyoming) [58] have adopted the use of diaryl disulphane solvents for removing elemental sulphur from wells and flowlines. As a result, preliminary investigations on the stability of diaryl polysulphanes, the product of sulphur uptake by diaryl disulphane solvents, were conducted.

The thermal decomposition of 100 wt% sulphur-loaded diaryl polysulphanes,  $(4-CH_3C_6H_4)_2S_X$ ), having an average value of x = 5, was carried out at 150° and 200°C for 15 days in an open system. The progress of the reaction was followed by reverse-phase HPLC and by proton-decoupled ¹³C NMR . Figures 3.11 and 3.12 compare the changes in the HPLC chromatograms and the ¹³C NMR spectra, respectively, of the starting polysulphane and the polysulphane maintained at 150° or 200°C for 15 days.

A careful analysis of the chromatograms of the polysulphane mixtures gave no direct evidence that decomposition of the diaryl polysulphanes had occurred (Figure 3.11). The results, however, indicated that larger diaryl polysulphanes,  $((4-MeC_6H_4)_2S_X)$ , with x = 13 - 17) with higher x value had been formed. This can be compared with the starting diaryl polysulphane for which a maximum value of x = 12 was observed.

The existence of long chain polysulphanes with x > 5 cannot be established with certainty. This is because individual polysulphanes containing more than 6 sulphur atoms have yet to be isolated because of their tendency to disproportionate during analysis. In fact, considerable effort was made to isolate and characterize each peak corresponding to x = 6 - 12 using preparative reverse phase chromatography. However, re-analysis of material collected from elution of a "single peak" gave a series of peaks corresponding to the original polysulphanes. This is consistent with the disproportionation of dimethyl polysulphanes described by Wajon *et al* [7]. It is therefore not an easy task to unambiguously assign all the observed chromatographic peaks. However, by assuming that each peak in the chromatograms corresponds to polysulphanes (with the exception of elemental sulphur) with one sulphur atom added to the chain, and that each additional sulphur atom contributes to an increased retention time, then by counting the peaks, it is reasonable to suggest the existence of (4-CH₃C₆H₄)₂S₁₇, although as indicated in Fig. 3.11, it is only present in trace quantities.



HPLC Chromatogram of *Bis*(4-methylphenyl) Polysulphane: (a) mixture obtained at 20°C, (b) after heating for 15 days at 150°C Figure 3.11

(a)

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The ¹³C NMR investigations gave results consistent with those of the HPLC analysis. There seems to be little difference between the NMR spectra of the starting diaryl polysulphane and the polysulphane which had been heated at 150° or 200°C for 15 days (Figure 3.12). There were changes in relative intensities of the signals, but no new signals appeared. This suggests that the polysulphanes did not decompose at these temperatures over the reaction time (15 days). Although tentative evidence for the formation of long chain polysulphanes with x = 17 was obtained from the HPLC analysis of the mixture, the results of NMR studies were inconclusive as ¹H and ¹³C chemical shift differences between individual diaryl polysulphanes were too small to discern higher polysulphanes. This parallels earlier observations on the NMR analysis of polysulphanes [36-37,57-58]. Thus only diaryl polysulphanes with x = 2 - 9 have been found to give resolved ¹³C NMR signals. The chemical shifts of the higher polysulphanes presumably converge at x  $\ge 9$  and become indistinguishable.

It was thought that 4-methylbenzenethiol might be formed as a decomposition product since the initial step involved in the thermolysis of organic polysulphanes is the homolytic cleavage of S-S bonds. The resulting 4-methylbenzenethio radical may subsequently abstract one of the methyl hydrogens to form the thiol. The fact that 4-methylbenzenethiol was not observed may be explained in terms of resonance stabilization of the 4-methylbenzenethio radical resulting from MeArS-S_xSArMe bond cleavage, thus making it less reactive to participate in hydrogen abstraction. The same results were obtained when 2- and 3-methyl derivatives of the diaryl polysulphanes were used.

The thermal decomposition of bis(4-methylphenyl) polysulphane was also carried out in the presence of a 100% hydrogen sulphide atmosphere in a closed system at 150° and 200°C for 48h reaction time. The results were similar to those described above. No 4-methylbenzenethiol formation was observed. From a mechanistic point of view, the following reactions leading to the formation of methylbenzenethiol were anticipated:



Figure 3.12 ¹³C NMR Spectra of *Bis*(4-methylphenyl) Polysulphane: (a) mixture obtained at 20°C, (b) after heating for 15 days at 150°C

$$CH_{3}C_{6}H_{4}S_{x}C_{6}H_{4}CH_{3} \xrightarrow{200^{\circ}C} CH_{3}C_{6}H_{4}S^{\bullet} + CH_{3}C_{6}H_{4}S^{\bullet}$$
(35)

$$CH_3C_6H_4S^{\bullet} + H_2S \longrightarrow CH_3C_6H_4SH + HS^{\bullet}$$
(36)

One explanation as to why the reaction represented by Equation 36 was not observed could be that any thiol produced was quickly converted back to the disulphane in the following equation:

$$2CH_3C_6H_4SH + 1/8S_8 \longrightarrow CH_3C_6H_4SSC_6H_4CH_3$$
(37)

The above findings suggest that diaryl polysulphanes, the product of sulphur uptake by diaryl disulphane, will be stable at conditions similar to those found in the sour natural gas downhole environments. Since 150°C is at the top end of temperatures found in most sour gas reservoirs (e.g. in Alberta), the above observations, in practical terms, indicate that diaryl disulphane would be suitable to mitigate the problem of sulphur deposition anticipated during the production of high hydrogen sulphide containing reservoirs.

### 3.7 CONCLUSION

The thermal decomposition study has shown that dimethyl polysulphane is unstable and will decompose to methanethiol and carbon disulphide as major products in an open reactor at temperatures greater than 50°C as well as to carbon disulphide and hydrogen sulphide in a closed reactor at temperatures in excess of 150°C.

For the open system experiments, the formation of methanethiol follows first order kinetics and an energy of activation of ca. 53 KJmol⁻¹ was estimated for the formation of methanethiol from DMPS. Closed system investigations suggest that the presence of hydrogen sulphide will reduce DMPS decomposition rates. However,

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regeneration of dimethyl disulphane solvent from DMPS will likely be uneconomical in view of the large losses of DMPS to the volatile  $CH_3SH$ ,  $CS_2$  and  $H_2S$ .

It has also been shown that bis(2,3,or 4-methylphenyl) polysulphane is more stable than dimethyl polysulphane under similar conditions, suggesting that bis(2,3,or 4-methylphenyl) disulphane may be a better solvent in handling the anticipated sulphur plugging when producing the deeper and hotter sour gas reservoirs.

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