CH_3SH conversion in a tubular flow reactor. Experiments and kinetic modelling

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Abstract

The use of non-conventional fuel sources, such as shale gas, brings new research requisites for its proper use in an environmental friendly manner. In this context, shale gas may include different sulphur containing compounds, such as methanethiol, that is also formed as intermediate during sulphur containing residues processing. The present work includes an experimental and kinetic modelling study of the oxidation of methanethiol, CH_3SH, in a quartz flow tubular reactor at atmospheric pressure and in the 300-1400 K temperature range. The influence of the temperature, the O_2 concentration and the presence of H_2O on the conversion regime of CH_3SH and the formation of different compounds has been analysed. The experimental results have been interpreted in terms of a detailed gas-phase mechanism compiled in the present work, and the elementary steps involved in the conversion of CH_3SH have been identified.

In general, oxidation of CH_3SH is favoured by both oxygen level and temperature, while the presence of H_2O does not modify the CH_3SH conversion profile. The main sulphur containing products are SO_2, H_2S and CS_2, pointing to a significant role of other products, apart from SO_2, for the control of pollutant emissions.

Keywords: *CH_3SH, methyl mercaptan, methanethiol, oxidation, sour gas, shale gas, PFR, kinetic modelling*

INTRODUCTION

The use of non-conventional fuel sources, such as shale gas, refinery gas, or biogas obtained from anaerobic digestion, brings new research requisites for its proper use in an environmental friendly manner. In this context, these gases, apart from CH_4 and CO_2, may include different sulphur containing compounds, such as hydrogen sulphide and mercaptans as methanethiol, that is also formed as intermediate during sulphur containing residues processing. The presence of sulphur in sour gases makes more difficult its application, mainly because of environmental issues. While the traditional way to use these fuels is based on their exhaustive cleaning [e.g. 1], the present strategies include the direct use of sour gases in combustion together with the improvement of technologies and combustion processes, along with the later solution of environmental problems. This is what has been named as a "double revolution" [2].

Methanethiol, CH_3SH, also known as methyl mercaptan, is a sulphur organic compound that can be present in a number of fuel gases, such as natural gas, sour gas, shale gas, biogas or refinery gas [3]. Formation of mercaptans (mainly CH_3SH), together with COS and CS_2 also occurs in the Claus process through the interaction of CO_2, hydrocarbon radicals and sulphur species [4], reducing thus the sulphur recovery efficiency. Shale gas has been reported to contain typically a total sulphur content of up to 1 %, including sulphur in pyritic form, sulfates and organics [5], with concentrations of mercaptans (CH_3SH) of up to 0.5 % [6]. CH_3SH can also be formed as an intermediate compound in the destruction of mustard gas, $ClCH_2$-CH_2-S-CH_2-CH_2Cl, through incineration mainly chosen as a high effectiveness destruction method, even though there is still significant concern over the potential formation of toxic emissions [7, 8]. Under oxidation conditions, conversion of CH_3SH may lead preferably to SO_2, but also to H_2S or other carbon-sulphur compounds such as COS or even CS_2.

While the conversion of COS and CS_2 have been considered in the past [e.g. 9-11], to our knowledge, no investigation of the oxidation of CH_3SH has been carried out under combustion conditions. However, significant efforts have been drawn to evaluate the oxidation of CH_3SH in the atmosphere, because of its probable and significant role in the atmospheric sulphur cycle (e.g. [12-14]). Actually, methanethiol has been reported to represent around a 10 % of the global flux of sulphur compounds in the atmosphere [15].

In this context, the present study aims to carry out a combined experimental and kinetic modelling study of the conversion of CH_3SH under combustion conditions. The impact of temperature and stoichiometry, ranging from almost pyrolysis to very oxidizing conditions, on the process is evaluated in a tubular flow reactor at atmospheric pressure and in the 300-1400 K temperature range. Experimental results are discussed in terms of a detailed kinetic mechanism. The present study is of interest in its own right, and may serve as a base case to consider the behavior of non-aromatic organic sulphur in combustion systems.

EXPERIMENTAL METHODOLOGY

Most of the experiments have been carried out in a quartz tubular flow reactor at atmospheric pressure. Only a brief experimental setup (setup 1) description is given here and a more detailed description can be found elsewhere [16]. The reactor has an isothermal reaction zone of 20 cm in length and 0.87 cm of internal diameter. Total flow rate in all experiments was 1 L (STP)/min, resulting in a gas residence time as a function of temperature of 194.6/T(K), in seconds. The reactor is placed in a three-zone electrically heated oven, ensuring a uniform temperature profile (±5 K) along the reaction zone. Experiments are carried out under highly diluted conditions using nitrogen as bath gas. Gases from cylinders are led to the reactor in up to four separate streams, following the procedure of Alzueta et al. [17], and are heated separately and mixed in cross flow at the reactor inlet. At the outlet of the reaction zone, the product gas is quenched by means of external cooling air. The exhaust gases go

through a condenser and a filter, removing any possible residual solid and moisture, and subsequently conducted to the analysis system, which includes a UV continuous analyser for SO_2, an IR continuous analyser for CO and CO_2 and a gas micro-chromatograph for CH_3SH, H_2S, COS, CS_2, CH_4, CO, CO_2, O_2 and H_2 quantification. The uncertainty of the measurements is estimated within 5 %.

Additionally, with the purpose of evaluating a strange behavior found in CO formation that will be described later in detail, one experiment has been performed in a different installation (setup 2) that is described in a previous work by our group [18].

KINETIC MODEL

The experimental results have been interpreted in terms of an updated kinetic model. The mechanism used is based on the mechanism by Alzueta et al. [19] developed to analyse the impact of the presence of SO_2 on fuel conversion, and includes the interaction of SO_2 with CO and small hydrocarbons by Glarborg et al. [20, 21]. This mechanism was later updated by Giménez-López et al. [22] to account for oxy-fuel combustion conditions. To the updated mechanism, we have added a CH_3SH conversion subset, and related thermochemistry, taken mainly from the works of Zheng et al. [7, 23] and Van de Vijver et al. [24], who studied respectively the oxidation of diethyl sulphide and the pyrolysis of alkyl sulphides. The work of Van de Vijver et al. [24] is, in turn, largely based on previous works by the group [25-29]. This reaction subset has also been largely used in the recent work of Gersen et al. [30], who studied the effect of H_2S addition on methane ignition and oxidation at high pressure. Subsets for COS and CS_2 conversion were taken from previous works from the authors [31, 32] and the H_2S conversion subset from a recent work by our group [33]. This H_2S reaction subset is largely based on the works of Sendt et al. [34], Zhou et al. [35] and Song et al. [36]. The mechanism of Colom-Díaz et al. [33] included the isomerization of HSOO to HSO_2, as a key fast step for H_2S oxidation, together with new kinetic parameters for the $SH+H_2O_2 \leftrightarrows H_2S+HO_2$ reaction, which was found to have a significant impact on H_2S conversion, and that is included in the present mechanism, since the formation of significant amounts of H_2S from methanethiol can be expected.

The final reaction mechanism listing is included as supplementary material. As for thermochemical data, same sources as for the corresponding reactions were used. Calculations were carried out using the PFR model of the Chemkin Pro suite [37].

RESULTS AND DISCUSSION

The study of CH_3SH oxidation in a tubular flow reactor at atmospheric pressure has been carried out from almost pyrolysis to fuel-lean conditions, in the temperature range of 300-1400 K. The experimental conditions studied are listed in Table 1. The influence of the amount of oxygen available on the process was studied for different values of λ, defined as O_2(real)/O_2(stoichiometric). For an inlet total flow rate of 1 L (STP)/min, the gas residence time in the reactor varies in the 0.14-0.24 seconds range depending on temperature, according to 194.6/T(K), with the exception of experiment 8, for which the residence time is 414/T(K) seconds.

Table 1: Experimental conditions. Experiments 1 to 7 are performed at atmospheric pressure in setup 1 [16]. Experiment 8 is performed at 1.81 bar in setup 2 [18].

Set	CH_3SH (ppm)	O_2 (ppm)	H_2O (%)	λ	Setup
1	983	42	-	0.01	1
2	968	1211	-	0.42	1
2a	972	979	0.5	0.34	1
3	977	2269	-	0.77	1
4	952	2841	-	0.99	1
4a	1003	2953	0.5	0.98	1
4r	965	2841	-	0.98	1
5	965	4576	-	1.58	1
6	973	5878	-	2.01	1
7	973	14855	-	5.08	1
7a	1015	13370	0.5	4.39	1
8	987	3025	-	1.02	2

For the conditions listed in Table 1, the concentrations of CH_3SH, SO_2, H_2S, O_2, CO, CO_2, H_2, CH_4 and CS_2 obtained as a function of temperature are presented in Figure 1.

Figure 1 shows the experimental results for the quantified species during the conversion of CH_3SH as a function of temperature and for the different stoichiometries studied (λ values ranging from almost pyrolysis conditions to very fuel-lean conditions), in the absence of water. Experimental sulphur and carbon mass balances close to 100±5 % in most cases, except for carbon at intermediate temperatures (823-923 K) were the balance goes down to 70-75 %. This is attributed to the fact that the sharpest conversion of CH_3SH occurs in this temperature interval, with many intermediates in small concentrations that appear and are not quantified.

Methanethiol starts its conversion between 800 and 1000 K as a function of stoichoimetry, with the onset conversion temperature shifted towards lower temperatures as the oxygen availability in the reaction environment is higher. Most of CH_3SH conversion occurs in a narrow temperature range of about 50 K. The final products dominant in CH_3SH conversion include H_2, CO, CO_2, and SO_2 as sulphur species. With the exception of CO and SO_2 (under fuel-rich conditions), which exhibit a maximum as a function of temperature, the rest of dominant final products increase with temperature under the conditions considered. It is worthwhile to mention that, for the highest temperatures (above 1000 K approximately) and the fuel leaner stoichiometries (λ=1.5 and above), the sulphur present in CH_3SH is fully converted to SO_2. For λ<1, conversion of CH_3SH also results in the formation

of intermediates, as CH_4 and H_2S, which exhibit a maximum that is shifted to lower temperatures, as the stoichiometry becomes fuel leaner. It is noticeable that, under the fuel-rich conditions studied, CH_4 and H_2S are still present even at the highest temperatures considered. It is also remarkable that CS_2 is formed in all the experiments, appearing in significant concentrations under fuel-rich conditions, while COS (O=C=S) was found in the range of few ppm, only under reducing conditions (λ<0.7) and at the highest temperature considered in the present study. This is in agreement with earlier studies [31], where the formation of COS has been reported to be formed in the oxidation of CS_2. Under reducing conditions, the formation of a yellow powder was observed at the outlet of the reactor, but its quantification was not possible, as also happened in previous works by our group [33]. The kinetic model used in the present work also predicts the formation of small amounts of S_2 under reducing conditions.

The results shown in Figure 1 correspond to experiments performed in the absence of water vapour. In order to evaluate the impact of the presence of water, which has been reported to shift the conversion of CO in the presence of SO_2 [20], experiments in the presence of water (0.5 %) have been performed, and the results obtained in both the absence and presence of water are shown in Figure 2. As an example, for fuel-rich conditions, Figure 2a shows that the results with and without water are very similar for all the species measured, despite the slight differences between the two experiments in relation to the initial concentrations of CH_3SH and O_2 (968 and 972 ppm, and 1211 and 979 ppm, respectively), which result in a slightly different λ value (0.42 and 0.34 respectively), and the slightly different pressures (1 and 1.8 bar respectively). Similar findings were obtained for other stoichiometries (Figures 2b and 2c). From these results, and under the conditions considered in the present work, no impact of water presence on the conversion of CH_3SH can be drawn.

In order to further explore the performance of the experiments, Figure 3 shows an example of the repeatability of experiments for the case of λ=1. The results show a good repeatability of all the different species concentrations measured, and the slight differences observed can be attributed to the non-exactly equal initial conditions of experiments 4 and 4r in Table 1.

As has been mentioned earlier, we have used a chemical detailed mechanism to interpret the experimental data of methanethiol conversion under the studied conditions in the present work. Figure 4 shows, as an example, the comparison between the experimental results and calculations for three selected stoichiometries (fuel-rich: λ=0.77, stoichiometric: λ=0.99, and fuel-lean: λ=5.08, sets 3, 4 and 7 in Table 1). Symbols represent experimental data and lines indicate model predictions using the mechanism compiled in this work. As seen, the model reproduces fairly well both the tendencies and the concentrations of the different compounds, through all the temperature range considered and for the different stoichiometries, with the exception of CO at temperatures below approximately 1200 K. A similar agreement is obtained for the rest of stoichiometries studies, not shown.

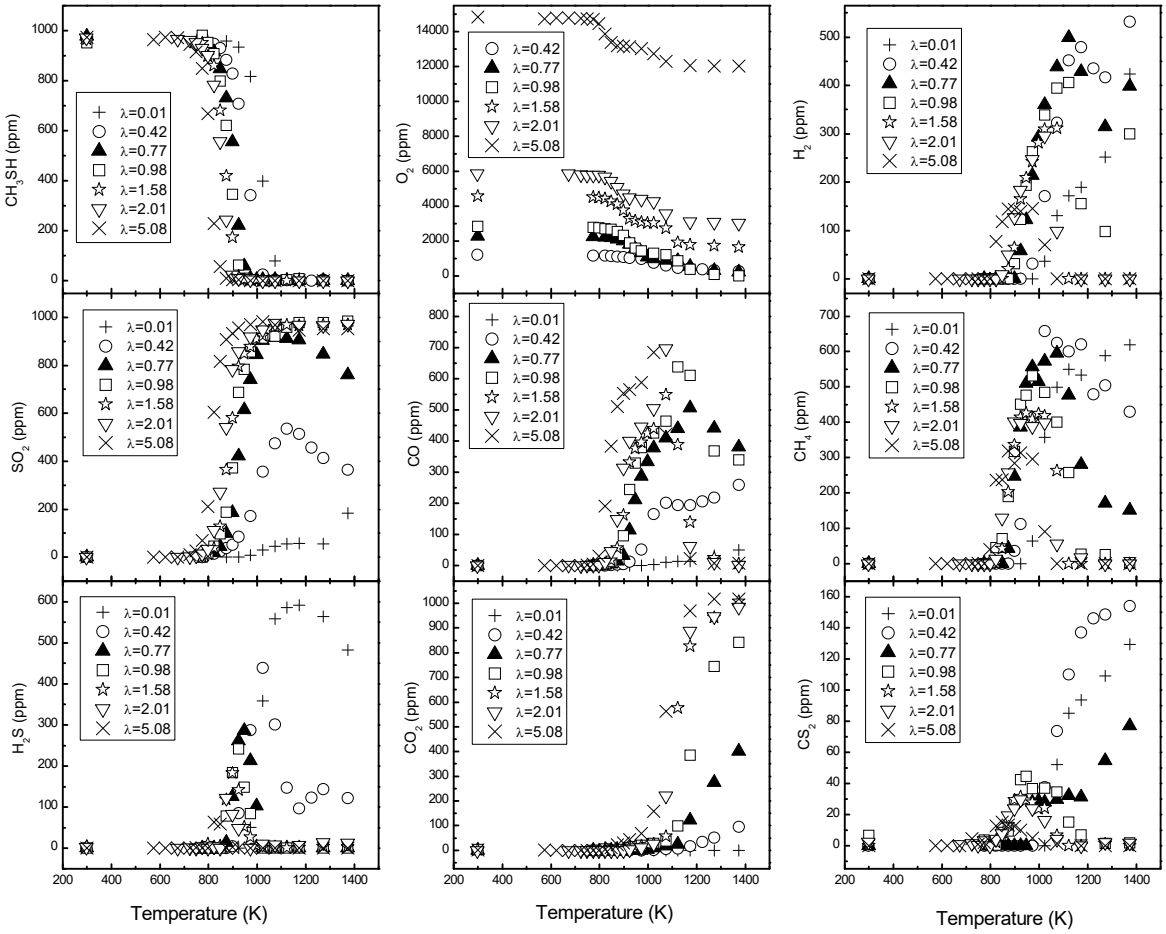

Figure 1. Experimental concentrations of CH_3SH, SO_2, H_2S, O_2, CO, CO_2, H_2, CH_4 and CS_2 as a function of temperature for different stoichiometries. Results correspond to sets 1 to 7 in Table 1.

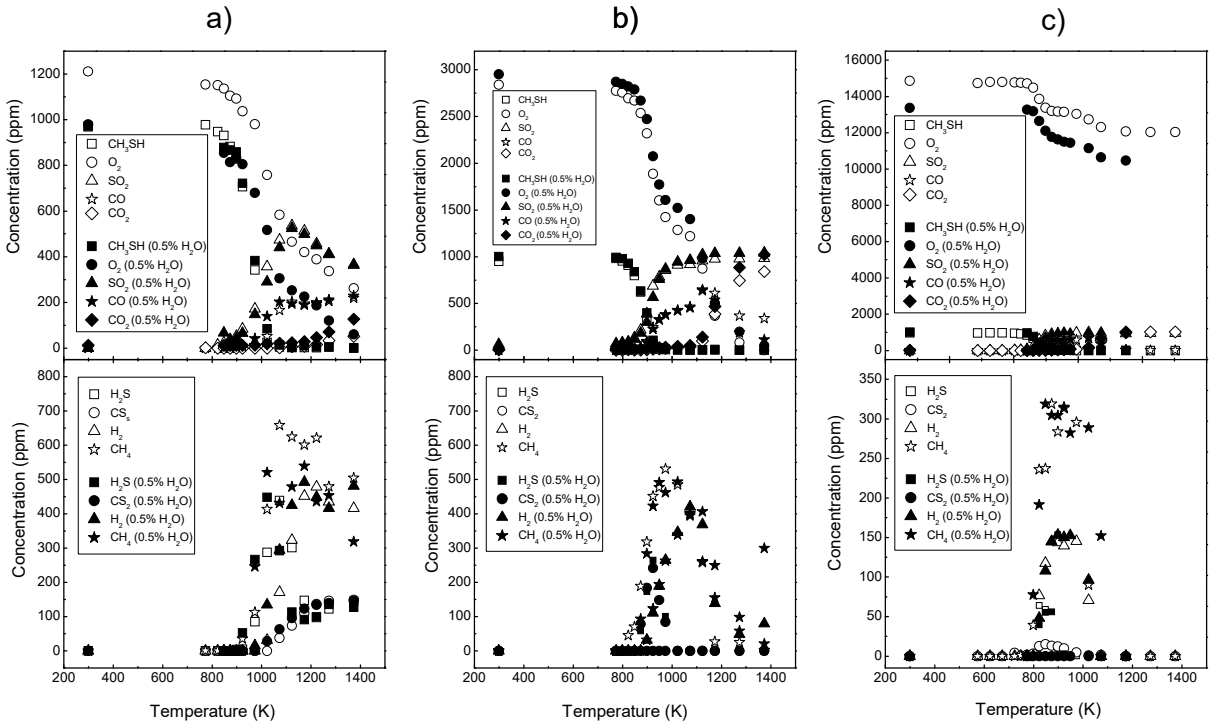

Figure 2. Experimental concentrations of CH_3SH, SO_2, H_2S, O_2, CO, CO_2, H_2, CH_4 and CS_2 as a function of temperature both in the absence and presence of water (0.5 %) and for rich, stoichiometric and fuel-lean conditions. Results of a) graphs correspond to sets 2 and 2a (fuel-rich conditions); results of b) graphs correspond to sets 4 and 4a (stoichiometric conditions); and results of c) graphs correspond to sets 7 and 7a (fuel-lean conditions) in Table 1.

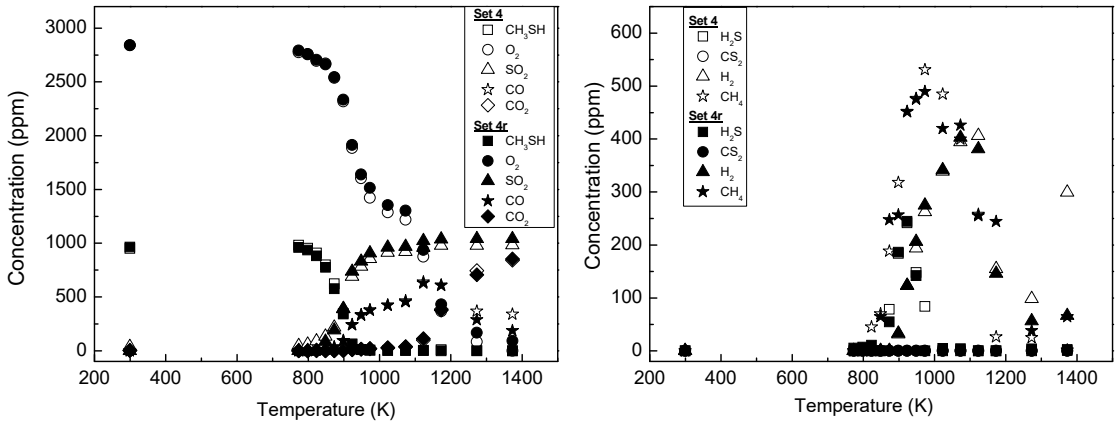

Figure 3. Example of the repeatability of experiments. Experimental data correspond to experiments 4 and 4r in Table 1.

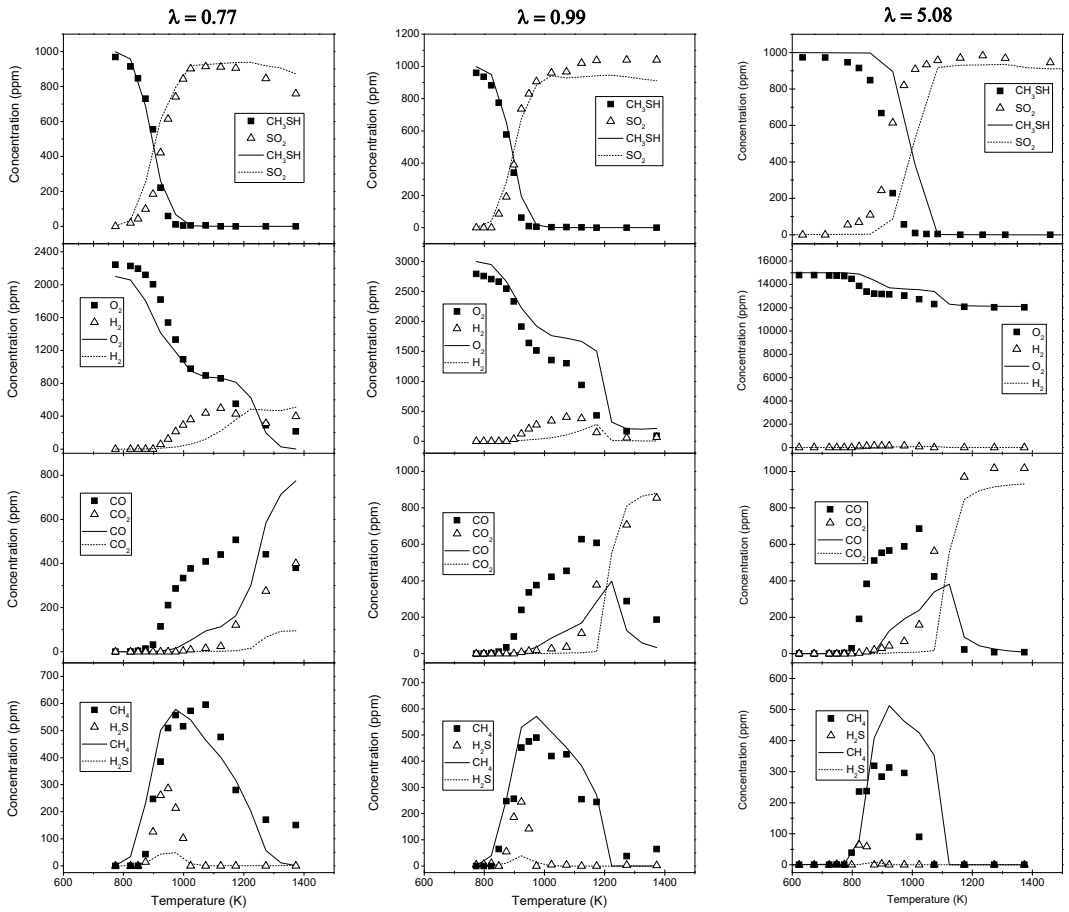

Figure 4. Comparison between simulations and experimental results for λ=0.77 (set 3 in Table 1), λ=0.99 (set 4 in Table 1), and λ=5.08 (set 7 in Table 1).

While the experimental CO concentration exhibits an early formation coinciding with CH_3SH diminution, the model does not capture this behaviour. It has to be mentioned that the concentration of CO in the experiments was measured simultaneously by a continuous IR analyser and by gas chromatography, and identical results were obtained. Additionally, we also performed some selected FTIR measurements and the FTIR CO determinations coincided with the CG and continuous analysers. Therefore, and in order to further prove if this early experimental CO formation is an experimental artifact or a phenomenon effectively occurring during CH_3SH conversion, we decided to do an additional experiment in a different experimental setup [18], which has been used with success in other studies addressing sulphur chemistry (e.g. [33]). This setup, which has significantly different dimensions compared to the one used in the rest of experiments, includes a flow tubular reactor where reactants enter premixed. The results of this experiment (experiment 8 in Table 1), together with model calculations, are shown in Figure 5. It can be observed that, despite the differences in the experimental conditions and installation used, the model can reproduce the experimental observations with the exception of the concentration of CO in the 800 to 1200 K temperature range, where the same early formation of CO is attained. Thus, from these results, we can conclude that the early formation of CO effectively occurs. However, we are not able to predict this early CO formation with the current knowledge of the chemistry addressing the conversion of CH_3SH and other thiols.

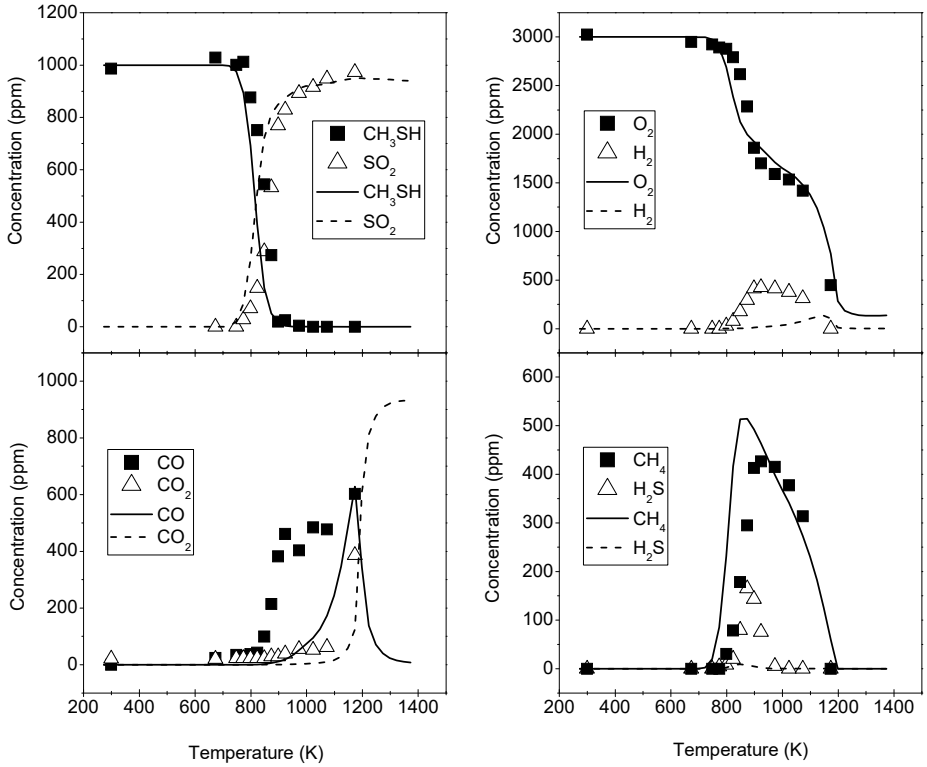

Figure 5. Experimental and simulated results of experiment 8 in Table 1.

Figure 6 includes a reaction pathway diagram of CH_3SH conversion. At the beginning of reaction, CH_3SH is mainly decomposed or consumed by reaction with O_2 (R1 and R2), with a minor contribution of thermal decomposition (R3),

$CH_3SH+O_2 \rightleftharpoons CH_2SH+HO_2$ (R1)

$CH_3SH+O_2 \rightleftharpoons CH_3S+HO_2$ (R2)

$CH_3SH \rightleftharpoons CH_3+SH$ (R3)

SH radicals contribute to S and S_2 formation, which appear to be relevant for CS_2 formation, as stated further below. A small fraction of SH radicals reacts with oxygen and follows the typical oxidation pathway for this species, as shown in Colom-Díaz et al. [33]. The SH radicals formed in reaction R3 also participate in a minority pathway, reacting with C_2H_4, which in turn is formed from ethane generated from CH_3 recombination, leading to CH_2CH_2SH, which participates in an isomerization cycle to CH_3CH_2S and goes back to CH_2CH_2SH.

Apart from the CH_3SH+O_2 reaction, as soon as methyl radicals are formed (e.g. reaction R3), they react with CH_3SH leading to the formation of two isomers, CH_3S and CH_2SH, (reactions R4 and R5):

$CH_3SH+CH_3 \rightleftharpoons CH_3S+CH_4$ (R4),

$CH_3SH+CH_3 \rightleftharpoons CH_2SH+CH_4$ (R5),

and once the O/H radical pool builds up, reactions with radicals also occur (R6-R9), with reaction (R6) as the dominant one:

$CH_3SH+OH \rightleftharpoons CH_3+H_2SO$ (R6)

$CH_3SH+H \rightleftharpoons CH_3S+H_2$ (R7)

$CH_3SH+O \rightleftharpoons CH_3S+OH$ (R8)

$CH_3SH+HO_2 \rightleftharpoons CH_3S+H_2O_2$ (R9)

The CH_3SH subset was taken entirely from the work of Van der Vijver et al. [24], which was developed for the thermal decomposition of diethyl sulphide and ethyl methyl sulphide using a rule based kinetic model generator Genesys, with certain modifications as discussed later, and from the works of Zheng et al. [7, 23] of their studies on ethyl methyl sulphide and diethyl sulphide oxidation. As seen, the mechanism describes properly methanethiol conversion and, thus, it can be considered as appropriate.

The methyl thiyl radical (CH_3S), which is formed in considerable amounts mainly through reaction R4, basically reacts with O_2, independently of the stoichiometry. The CH_3S+O_2 reaction has three product channels (R10-R12):

$CH_3S+O_2 \rightleftharpoons CH_2S+HO_2$ (R10)

$CH_3S+O_2 \rightleftharpoons CH_3+SO_2$ (R11)

$CH_3S+O_2 \rightleftharpoons CH_3SO+O$ (R12)

with the first two ones dominant under the conditions of the present work.

For this reaction ($CH_3S+O_2 \rightarrow$products), there are only experimental room temperature upper-limit determinations [38, 39]. More recently, the reaction was studied by Zhu and Bozzelli [40], who analysed a number of possible reaction channels for this reaction relevant for atmospheric chemistry by means of DFT and ab initio methods, and isolated the dominant channels which appear to be those mentioned above. In the present work, the determinations of Zhu and Bozzelli [40] for this reaction rate have been adopted.

CH_2SH, formed in reaction R1, is mainly converted into the CH_2S radical by reaction with oxygen,

$CH_2SH+O_2 \rightleftharpoons CH_2S+HO_2$ (R13)

for which the rate constant provided by Zheng et al. [23] has been used.

CH_2S is an important intermediate, originated from both CH_3S and CH_2SH (reactions R10 and R13, respectively). Once formed, CH_2S reacts with the O/H radical pool and also with CH_3 radicals, which are present in significant amounts for all the conditions studied, through reactions R14-R17, giving CHS.

$CH_2S+H \rightleftharpoons CHS+H_2$ (R14)

$CH_2S+O \rightleftharpoons CHS+OH$ (R15)

$CH_2S+OH \rightleftharpoons CHS+H_2O$ (R16)

$CH_2S+CH_3 \rightleftharpoons CHS+CH_4$ (R17)

CS_2 is formed through the reaction of CHs with S or S_2, formed from SO and SH, in reactions R18 and R19:

$CHS+S \rightleftharpoons CS_2+H$ (R18)

$CHS+S_2 \rightleftharpoons CS_2+SH$ (R19)

CS_2 is finally directly converted into SO_2. Compared to the $CH_3S+O_2 \rightleftharpoons CH_3+SO_2$ reaction path forming SO_2, the $CH_3SH \rightarrow CH_2SH/CH_3S \rightarrow CH_2S \rightarrow CHS \rightarrow CS_2 \rightarrow SO_2$ sequence is more relevant as the stoichiometry becomes fuel richer, being dominant for the richest conditions studied in the present work.

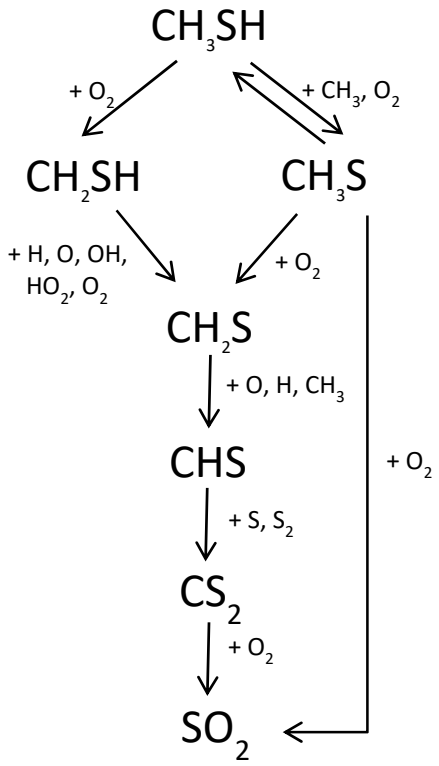

Figure 6. Main reaction pathway diagram of CH_3SH conversion to SO_2.

Figure 7 shows, as an example, the sensitivity analysis performed for CH_3SH, at λ=0.99, at the temperature of 798 K and at the outlet of the reaction zone. As seen, the results are mainly sensitive to the CH_3SH+CH_3 reaction producing CH_2SH, which is an important conversion pathway for CH_3SH once conversion has been initiated, and the dominant one under rich conditions. Reactions of CH_3SH+CH_3 have been taken from the mechanism of Gersen et al. [30] and were also included in the mechanism of Zheng et al. [23], used for the study of diethyl sulphide oxidation with success and to evaluate the pyrolysis and oxidation of sulphur mustard simulates [41]. The kinetic parameters of the CH_3SH+CH_3 reaction are theoretical estimates. Therefore, since these reactions appear to show a significant sensitivity under the studied conditions of this work, a proper determination of them, not available at present, would be desirable. Also, reactions controlling the radical H/O and CH_3 pool appear to exhibit a high senstivity on the model calculations for both CH_3SH and CO, which are representative of the full oxidation process of methanethiol. Similar results, not shown, are obtained for other stoichiometries considered.

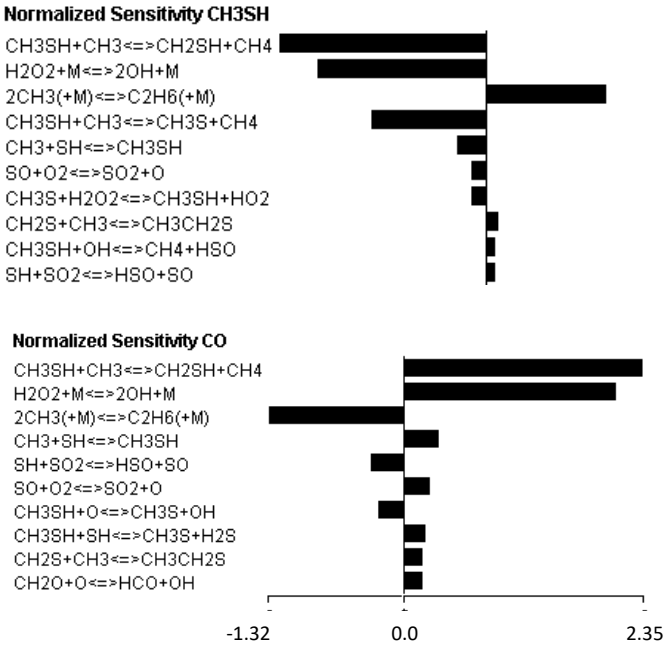

Figure 7. Normalized sensitivity analysis results for CH_3SH and CO, for λ=0.99 (set 4 in Table 1) at the outlet of the reaction zone at the temperature of 798 K.

CONCLUSIONS

Oxidation of CH_3SH at atmospheric pressure has been studied under different reaction atmospheres, varying the air excess ratio (λ) from almost pyrolytic conditions (λ=0.01) to oxidizing conditions (λ=5.08). The experiments were carried out in a quartz tubular flow reactor, in the 300-1400 K temperature range and concentrations of CH_3SH, H_2S, SO_2, COS, CS_2, CH_4, H_2, O_2, CO and CO_2 were determined. CH_3SH conversion starts between 800 and 1000 K, shifting toward lower temperatures as λ is higher, and most of the conversion occurs in a narrow temperature window. The results obtained with and without water vapour are similar for all the species measured. The main products of CH_3SH conversion appear to be H_2, CO, CO_2 and SO_2, with a remarkable formation of CS_2, while COS only was detected under reducing conditions (λ<0.7) and at the highest temperatures studied.

A detailed kinetic mechanism for the conversion of CH_3SH under the present conditions has been compiled based on different literature reaction subsets, and has been used to simulate the experimental results obtained in the present work, with a general good agreement between experimental results and simulations. The exception is the failure in the mechanism to predict the experimentally early CO formation found, for all the conditions studied, and from experiments carried out in different experimental installations. Additionally, the mechanism has been used to identify the main reactions governing the conversion of CH_3SH and the reactions to which the results are more sensitive.

ACKNOWLEDGEMENT

The authors express their gratitude to Aragón Government and European Social Fund (GPT group), and to MINECO and FEDER (Project CTQ2015-65226) for financial support. The assistance of J.M. Colom-Díaz with the experimental setup 2 is highly acknowledged.

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