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Q1

H_2S conversion in a tubular flow reactor: Experiments and kinetic modeling

Q2

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Abstract

Oxidation of H_2S at atmospheric pressure has been studied under different reaction atmospheres, varying the air excess ratio (λ) from reducing ($\lambda = 0.32$) to oxidizing conditions ($\lambda = 19.46$). The experiments have been carried out in a tubular flow reactor, in the 700-1400 K temperature range. The concentrations of H_2S, SO_2 and H_2 have been determined and the experimental results have been simulated with a detailed chemical mechanism compiled in the present work. The experimental results obtained indicate that H_2S consumption is shifted to lower temperatures as the stoichiometry increases, starting at 925 K for reducing conditions and at 700 K for the most oxidizing ones. The model reproduces well, in general, the experimental data from the present work, and those from the literature at high pressures. Supported by theoretical calculations, the isomerization of HSOO to HSO_2 has been determined as an alternative and possible pathway to the final product SO_2, from the key $SH + O_2$ reaction.

Keywords: H_2S; Oxidation; Sour gas; PFR; Kinetic modeling

1. Introduction

Conventional natural gas, as well as different non-conventional fuel mixtures or biogas generated in anaerobic digestion, may contain different amounts of hydrogen sulfide (H_2S) in their composition. Additionally, hydrogen sulfide can also be found as a by-product from the oil industry, released from the pyrolysis of fuels containing sulfur, natural gas cleaning or in synthesis gas produced from gasification of coal and biomass. Due to the corrosive and harmful nature of hydrogen sulfide, streams containing H_2S are led to cleaning treatments (e.g., amine absorption) and sulfur recovery units, which convert hydrogen sulfide into sulfur through the Claus process. This process is divided in two reaction steps: in the first one (thermal step), H_2S undergoes a partial oxidation in air, and then in the second one, it reacts with SO_2 to form sulfur in the presence of a catalyst (catalytic step) [1–3].

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As the energy demand increases worldwide, an efficient utilization of available natural resources is needed. The increasing importance of fuel sources, such as sour and shale gas (up to 30% of hydrogen sulfide content in volume), brings interest to the direct use of these fuels without the use of expensive cleaning treatments and to devote the main effort to the development of technologies and combustion processes [4]. The different fuel compositions, together with the presence of different combustion atmospheres, may affect the conversion of H_2S. In this context, it is interesting to be able to predict the most appropriate conditions for stable combustion at the desired temperatures, with minor pollutant emissions.

However, the oxidation steps chemistry of H_2S remains unknown in many aspects, and the available experimental data are limited. In 2000, Gardiner et al. [5] reviewed the significant progress in the understanding of the kinetics and mechanisms of the atmospheric oxidation chemistry of sulfur in the last decades, indicating the less effort placed on developing and understanding sulfur combustion kinetics. More recent studies have faced different combustions chemistry studies. For example, Bongartz and Ghoniem [6] developed an optimized mechanism to make predictions on the combustion behavior of sour gas under oxy-fuel conditions. In the same way, Cong et al. [2] developed a mechanism to assess the production of hydrogen through H_2S thermolysis for the Claus process. Despite these efforts, there is still a need for more accurate direct determination of several important rate constants as well as more validation data [6].

Additionally, there are also experimental works involving H_2S oxidation. For example, earlier investigations at high temperatures [7], H_2S mixtures explosion limit determinations [8], induction time measurements in reflected shock waves [9] or premixed flames [10], have been performed. Besides, recent researches in flow reactors, more related to this study, include the work of Zhou et al. [11], who performed experiments of H_2S oxidation in a flow reactor at atmospheric pressure, under fuel-lean conditions and in the temperature range of 950–1150 K. In another study, Song et al. [12] conducted experiments at high pressures (30–100 bar), evaluating the oxidation of H_2S under oxidizing and stoichiometric conditions, concluding that the combustion behavior depends strongly on the stoichiometry and pressure.

In this context, the present study aims to extend the results available in the literature related to H_2S conversion, and addresses the oxidation of H_2S under different stoichiometries, ranging from fuel-rich to fuel lean conditions. Experimental work in a tubular flow reactor at atmospheric pressure has been performed, in the temperature range of 700–1400 K. A kinetic model developed by our group, updated for this work, has been used to simulate the experimental results.

2. Experimental methodology

The experiments have been carried out in a quartz tubular flow reactor at atmospheric pressure. Only a brief experimental setup description is given here and a more detailed description can be found elsewhere [13]. The reactor has a 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. Besides, heat release from chemical reactions is minimized by performing the experiments under highly diluted conditions and using nitrogen to balance. Gases from gas cylinders are led to the reactor in up to four separate streams, which are heated separately and mixed in cross flow at the reactor inlet. At the outlet of the reaction zone, using an external cooling air, the product gas is quenched. The flue gases are led to the analysis system previous pass through a condenser and a filter, that remove any possible residual solid and moisture, therefore a constant supply of clean dry combustion gases is delivered to the analyzers. The analysis instrumentation consists of a UV continuous analyzer for sulfur dioxide (SO_2) concentration measurements and a gas micro-chromatograph for H_2S and H_2 quantification. The uncertainty of the measurements is estimated within 5%.

3. Kinetic model

The experimental results were interpreted in terms of kinetic modeling, using an updated kinetic model based on earlier works by our group [14–16]. This updated model counted with a sub-set of sulfur chemistry reactions, but it was focused on SO_2 reactions. Therefore, additional hydrogen sulfide reactions have been added, taken mainly from the kinetic model by Song et al. for H_2S oxidation at high pressures [12]. The final reaction mechanism listing is included as supplementary material and can be obtained directly from authors. Modifications made in the present work are denoted as "present work: pw". As for thermochemical data, same sources as for the corresponding reactions were used. Calculations were carried out in the frame of Chemkin Pro with the PFR model [17].

Hydrogen sulfide reacts primarily with radicals like H, OH or HO_2 to form mainly SH radicals. In general, the reactions of H_2S with the radical pool have been determined either experimental and/or theoretically, and are known with certain confidence. The exception is the $H_2S + HO_2$ reaction, for which only an upper limit for the rate constant at room temperature is available [18]. This reaction has two different

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product channels: $H_2S + HO_2 \rightleftharpoons SH + H_2O_2$ and $H_2S + HO_2 \rightleftharpoons HSO + H_2O$. The uncertainty of the reaction kinetic parameters for the first channel and its high sensitivity have been previously mentioned elsewhere, especially in high-pressure works, where HO_2 radicals are expected to play a major role [12,19,20]. Scarce data referred to this reaction are available in the literature. There is also an experimental determination at room temperature for the reverse channel producing $SH + H_2O_2$ [21]. Available theoretical calculations include those by Zhou et al. [11] for the reversible $H_2S + HO_2 \rightleftharpoons SH + H_2O_2$ reaction, which was then lowered by a factor of 2 by Mathieu et al. [20], and calculations by Batiha et al. [22], indicating a much lower rate constant value. The recent work of Gersen et al. [19] on the effect of H_2S addition to methane ignition and oxidation at high pressures also identified the $H_2S + HO_2$ reaction to be important and claimed for the need of an accurate determination of its rate constant. Calculations in the present work were very sensitive to this reaction, in particular to the $SH + H_2O_2$ channel, and thus their kinetic parameters were estimated in the present work as $5 \cdot 10^{12}$ cm^3/mol s for the reverse reaction, i.e., $SH + H_2O_2 \rightleftharpoons H_2S + HO_2$. This estimation agrees well with the high temperature data of Zhou et al. [11] and Mathieu et al. [20], while it is considerably higher than the value of Friedl et al. [21], experimentally characterized at 298 K. The impact of this important reaction is further discussed in the "Results and discussion" section.

H_2S conversion mainly produces SH radicals. Subsequently such a diatom reacts and intermediate species are formed. This is considered as a key reaction step in the bibliography for H_2S combustion. Particular attention has been devoted to the $SH + O_2$ reaction [11,12,19,23,24] and significant differences concerning the rate constants and product channels of the $SH + O_2$ reaction have been reported in the literature. Stachnik and Molina [25] provided an upper limit rate constant for this reaction at 298 K of $2 \cdot 10^5$ cm^3/mol s. This reaction has been largely studied theoretically [11,26–29] and several product channels have been proposed, i.e., $HSO + O$, $S + HO_2$, and $SO + OH$.

Zhou and coworkers [11], in their atmospheric pressure study, indicated that the production of $SO + OH$ predominates at temperatures below 1000 K, while the formation of $HSO + O$ is the main pathway above this temperature. As will be seen later, these reactions are not very important for the conditions of the present work. Garrido et al. [26], in a high level ab initio study of the HSO_2 system, identified a new reaction channel for the $SH + O_2$ reaction, which would produce the preferred $SO_2 + H$ channel, via the HSO_2 intermediate. Song et al. [12] determined the kinetic parameters for the $SH + O_2 \rightleftharpoons SO_2 + H$ reaction through ab initio calculations, obtaining a rate constant of $1.5 \cdot 10^5 \cdot T^{2.1} \cdot e^{(-11{,}020/RT)}$ (cal, mol, cm^3, s). The inclusion of this reaction and corresponding kinetic parameters in the mechanism does not have any effect in the calculations under the conditions of the present work. Freitas et al. [27] mentioned that the connection between the intermediate structures, HSOO and HSO_2, takes place via an HSOO* isomer in an electronic excited state. HSOO has been reported to be formed in the $SH + O_2(+M) \rightleftharpoons HSOO(+M)$ reaction [26–30], while in some of these works the formation of HSO_2 and HOSO was considered to be inaccessible directly from $SH + O_2$. The fate of HSOO may include dissociation to $HSO + O$, but this reaction has been reported to have a significant energy threshold [28], and thus is not competitive. Following the work of Ballester et al. [31], where they studied the $SH + O_2$ reaction through quasi-classical trajectory (QCT) methods, HSOO may be considered to isomerize to HSO_2. Taking into account the barrier for HSO_2 formation determined by Freitas et al. [27], we assume an activation energy of 21.3 kcal/mol for the HSOO to HSO_2 isomerization. In this work, a reaction rate of $10^{17} \cdot e^{(-21{,}300/RT)}$(cal, mol, cm^3, s) has been proposed for this reaction. The impact of this assumption will be discussed later.

Table 1
Experimental conditions.

Set	H_2S (ppm)	O_2 (ppm)	λ
1	476	225	0.32
2	509	750	0.98
3	485	900	1.24
4	482	1500	2.07
5	492	3750	5.08
6	514	15000	19.46

4. Results and discussion

The study of H_2S oxidation in a tubular flow reactor at atmospheric pressure from fuel-lean to fuel-rich conditions, in the temperature range of 700–1400 K, has been carried out. The experimental conditions 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 s range.

For the conditions listed in Table 1, the concentrations of H_2S, SO_2 and H_2 obtained as a function of temperature are presented in Fig. 1. Symbols represent experimental data and lines model predictions using the mechanism compiled in this work. As seen, modeling predictions agree fairly well with the experimental data. Additionally, experimental sulfur mass balances

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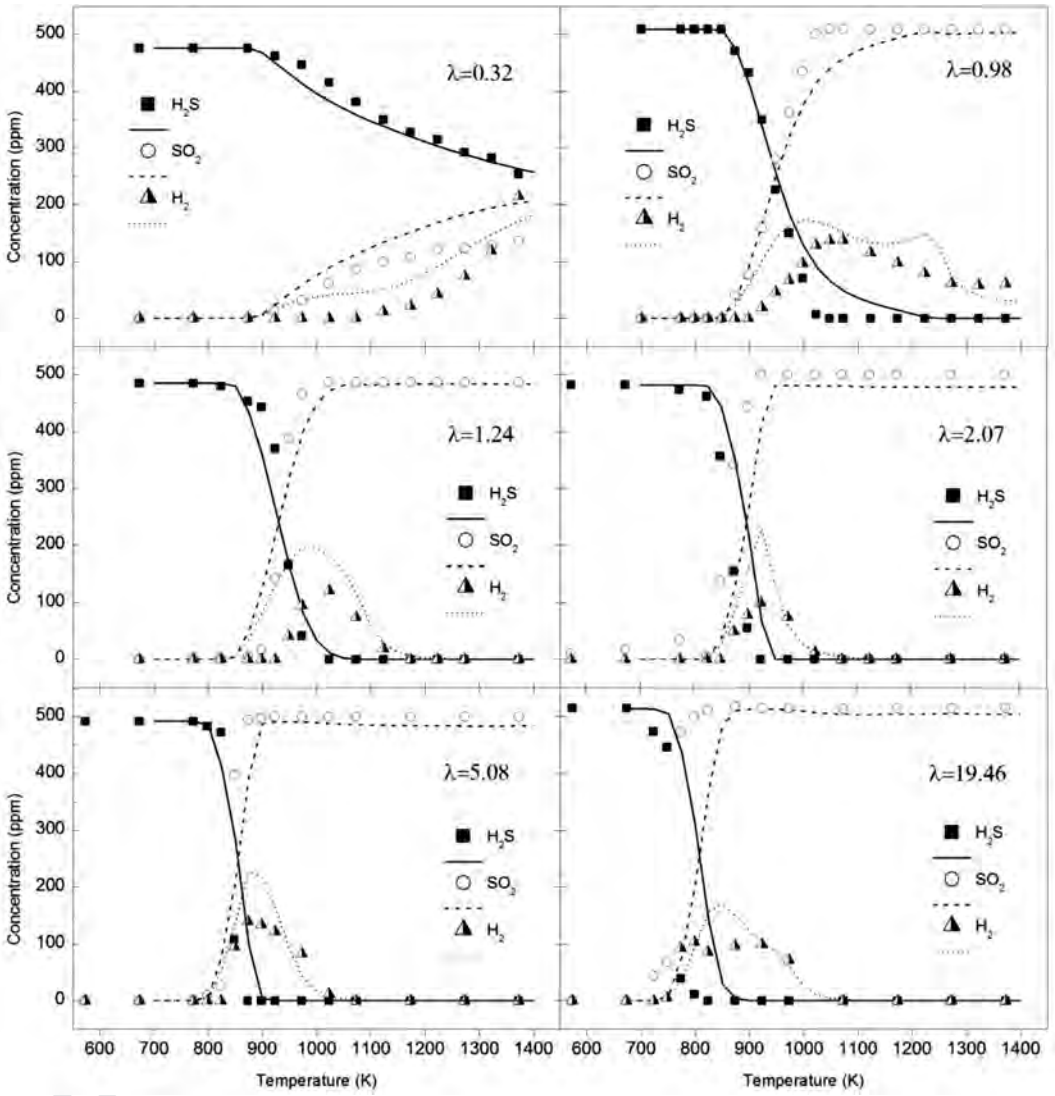

Fig. 1. Experimental results from H_2S oxidation in conditions of sets 1–6 in Table 1. Symbols represent experimental data and lines model predictions.

are shown in the supplementary material (Fig. S1), being close to 100% (±5 %) in most cases.

Hydrogen sulfide starts to react at 925 K under reducing conditions ($\lambda = 0.32$), with lower temperatures for the onset of H_2S consumption as the stoichiometry increases, dropping to 700 K for the highest oxygen concentration used ($\lambda = 19.46$). The onset of H_2S conversion is coincident with the onset for hydrogen and sulfur dioxide formation. H_2S is fully converted into SO_2 at high temperatures, except for the case of $\lambda = 0.32$, due to the lack of oxygen. Such a result was also observed in [32], where H_2S was neither consumed by the oxygen available nor by thermolysis. Under similar experimental conditions ($O_2/H_2S = 0.35$, 1375 K, $t_r = 150$ ms), but using 10% H_2S, Palma et al. [32] obtained 70% of H_2S conversion versus our 52% ($O_2/H_2S = 0.47$, 1375 K, $t_r = 140$ ms, 0.05% H_2S).

For $\lambda \geq 1$, when almost all H_2S is converted to SO_2, the H_2 formed starts to vanish. This was also observed by Zhou et al. [11], who mentioned that H_2 selectivity presents a maximum with the last traces of H_2S. The two maxima, observed for $\lambda = 0.98$ in H_2 predictions, are found to occur in the modeling by the concurrent formation and

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consumption of H_2. Hydrogen is formed mainly from H_2S and consumed by reaction with O/OH radicals. Once H_2S is fully consumed, the H_2 levels start to decrease at high temperatures.

A diagram showing the main reaction pathways is described in Fig. S2 of the supplementary material. Solid lines represent reaction paths at all stoichiometries, with the important species connected by thick arrows, and dashed lines correspond to additional reactions important only under reducing conditions. The most relevant pathways for H_2S oxidation show that the addition and modification of the reactions made in this work have a significant relevance in the oxidation behavior.

Calculations indicate that H_2S reacts with the radical pool (H, OH and HO_2), but primarily with H radicals, to rapidly form SH, independently of the stoichiometry. SH continues the reaction with O_2 to form mainly HSOO (R1), which isomerizes to HSO_2 (R2).

$$SH + O_2 (+M) \rightleftharpoons HSOO (+M) \quad (R1)$$

$$HSOO \rightleftharpoons HSO_2 \quad (R2)$$

Then, HSO_2 is branched to HOSO (R3) or to the final product SO_2 through (R4) and (R5), this last one under highly oxidizing conditions. HOSO, as well as HSO_2, can dissociate or react with oxygen (R6, R7). The reaction paths with S, SO and HS_2 radicals are quite similar to the ones identified by Zhou et al. [11], but less important in the present mechanism.

$$HSO_2 (+M) \rightleftharpoons HOSO (+M) \quad (R3)$$

$$HSO_2 (+M) \rightleftharpoons H + SO_2 \quad (R4)$$

$$HSO_2 + O_2 \rightleftharpoons SO_2 + HO_2 \quad (R5)$$

$$HOSO (+M) \rightleftharpoons SO_2 + H (+M) \quad (R6)$$

$$HOSO + O_2 \rightleftharpoons SO_2 + HO_2 \quad (R7)$$

The reaction process is maintained primarily by cause of H radicals released in the final step (R4), which maintain the consumption of H_2S through (R8), together with HO_2 radicals formed in (R7), which react with H_2S through (R9). Reaction (R9) becomes more important as the oxygen concentration increases, due to the major occurrence of (R5) and the increase in HO_2 concentration. The H_2O_2 radicals formed in (R9) decompose to OH radicals through (R10), promoting H_2S consumption through (R11).

$$H_2S + H \rightleftharpoons SH + H_2 \quad (R8)$$

$$H_2S + HO_2 \rightleftharpoons SH + H_2O_2 \quad (R9)$$

$$H_2O_2 (+M) \rightleftharpoons OH + OH (+M) \quad (R10)$$

$$H_2S + OH \rightleftharpoons SH + H_2O \quad (R11)$$

The production of HO_2 radicals through (R5) and (R7) makes reactions with this kind of radicals to become important, as for example (R9), which was found, together with (R2), to be the most sensitive under our experimental conditions at all stoichiometries. Figure S3 in the supplementary material shows, as an example, the sensitivity analysis for SO_2, obtained for $\lambda = 5.08$ at 823 K. Calculations indicate that the results are sensitive to the $SH + H_2O_2 \rightleftharpoons H_2S + HO_2$ reaction (-R9), which appears always as one of the top five most sensitive reactions. Therefore, we can confirm the necessity of having a good determination of the kinetic parameters of this reaction for an accurate modeling description. Results are also sensitive to the $HSOO \rightleftharpoons HSO_2$ reaction (R2), which has been proposed to occur and is included in the present mechanism. The impact of modifying the rate for (R2) is shown in Figs. S4 and S5 of the SM. Calculations indicate the necessity of including reaction (R2) in the model, even though the impact of varying the rate for (R2) is appreciable but not very significant.

Under reducing conditions, the consumption of H_2S follows the main reaction paths discussed in previous paragraphs. However, due to the lack of oxygen, other important species, such as H_2S_2, HS_2 and S_2, can be formed. S_2 can be produced through the sequence of reactions with SH (R12-R15), which self-reacts (R12) and forms HS_2, as well as with H_2S_2 (R13) formed by (R14). Finally, the HS_2 radical converts to S_2 through (R15). In the experiment carried out in the present work under reducing conditions, $\lambda = 0.32$, a yellow deposit was seen at the outlet of the reactor. In this experiment, for high temperatures, the mass balance for sulfur, which is calculated by adding the concentrations of H_2S and SO_2 measured at the reactor outlet, did not close, Fig. S1. Such unbalance can be explained by the presence of the yellow deposit, presumably S_2. The apparition of this deposit was also previously mentioned by Zhou et al. [11] and was attributed to the formation of S_2 in the gas phase, which condenses when exhaust gases are quenched.

$$SH + SH \rightleftharpoons HS_2 + H \quad (R12)$$

$$SH + H_2S_2 \rightleftharpoons HS_2 + H_2S \quad (R13)$$

$$HS_2 + HO_2 \rightleftharpoons H_2S_2 + O_2 \quad (R14)$$

$$HS_2 + SH \rightleftharpoons S_2 + H_2S \quad (R15)$$

In order to evaluate the model compiled in this work, we have performed simulations of literature results. In particular, we have simulated the flow reactor results from Song et al. [12] and Gersen et al. [19] of H_2S conversion at high pressures, where HO_2 radicals are important, and thus the impact of

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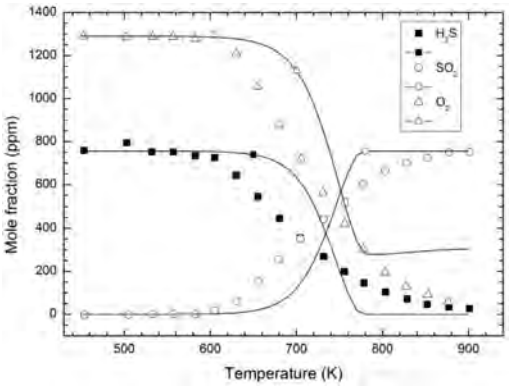

Fig. 2. Comparison of experimental data (symbols) of Song et al. [12] and simulations (lines) with the model developed in the present work. Stoichiometric conditions at 30 bar. Inlet composition: 756 ppm H_2S, 1290 ppm O_2, balance N_2 ($\lambda = 1.14$). The residence time in the isothermal zone is calculated from t_r (s) = 3520/T (K).

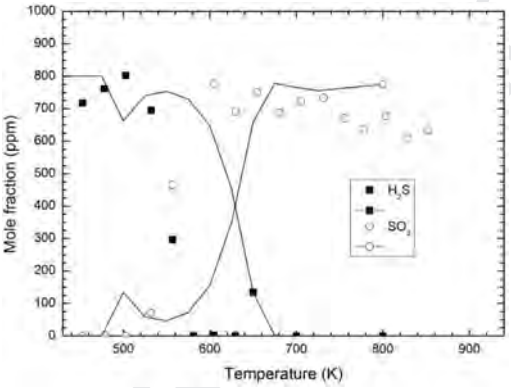

Fig. 3. Comparison of experimental data (symbols) of Song et al. [12] and simulations (lines) with the model developed in the present work. Oxidizing conditions at 30 bar. Inlet composition: 801 ppm H_2S, 4.4% O_2, balance N_2 ($\lambda = 36$). The residence time in the isothermal zone is calculated from t_r (s) = 3100/T (K).

(-R9) and its rate estimation may potentially be important. The simulation results are shown in Figs. 2 and 3 for the experiments of Song et al. [12] (stoichiometric and oxidizing conditions at 30 bar), and in Fig. 4 for the experiment of Gersen et al. [19] of H_2S/CH_4 oxidation (reducing conditions at 50 bar). In general, the present model reproduces well the main trends, and actually improves the previous predictions of the experimental results. The present simulation results are very similar to those obtained by Song et al. [12] under stoichiometric conditions, meanwhile, under oxidizing conditions, the authors were able to approximate the simulation results to

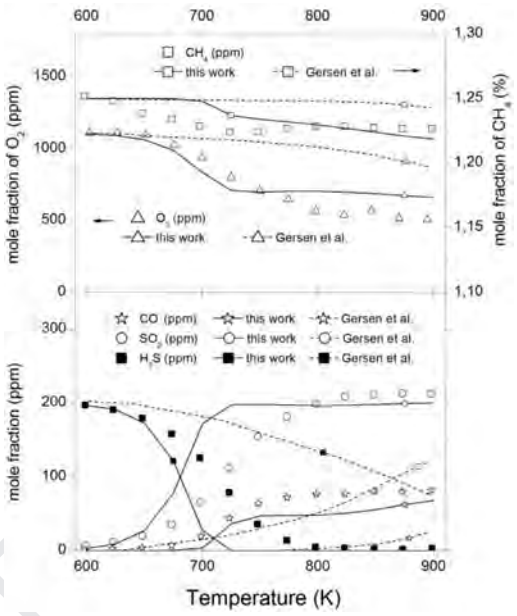

Fig. 4. Comparison between experimental data of Gersen et al. [19] (symbols) and model predictions (lines). Experiments with CH_4/H_2S in a flow reactor at 50 bar. Inlet composition: 1.25% CH_4, 1110 ppm of O_2, 200 ppm of H_2S, and balance N_2. The gas residence time is calculated as t_r(s) = 5990/T (K).

experimental ones by suppressing two reactions involving O_3 (R16 the most important one and R17), proposed by Mousavipour et al. [33]. The model in the present work keeps these reactions, which are found to be indeed important under the experimental conditions of Song et al. [12]. Reaction (R17) is a source of ozone and H_2S consumes it through (R16). Despite the scatter in the experimental SO_2 concentrations reported by Song et al. [12], the main trends in SO_2 evolution can be seen. Although, the simulation in Fig. 3 is 50 K shifted to higher temperatures compared to the experimental results, it is worthwhile to mention that the mechanism is able to reproduce the diminution in the observed H_2S mole fraction (ca. 480 K). Calculations indicate that the mentioned decrease between approximately 480 and 540 K occurs through the interaction between H_2S and O_3 (R16), which is the dominant consumption reaction of H_2S at these temperatures. Above 500 K, reaction (R16) becomes less important because of the decrease in the O_3 concentration, and H_2S conversion proceeds mainly through reaction (R9).

$$H_2S + O_3 \rightleftharpoons SO_2 + H_2O \quad \text{(R16)}$$

$$SH + O_2 + O_2 \rightleftharpoons HSO + O_3 \quad \text{(R17)}$$

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Figure 4 includes the simulation results of both the model of Gersen et al. [19] and the present model at 50 bar. Simulation of the combustion behavior of CH_4/H_2S and formation of products is improved with the present mechanism, which predicts well the tendencies. Under these conditions, H_2S reacts to SO_2 through the SH reaction channel (R1 and R2). In the case of CH_4/H_2S oxidation, the model predicts that CO starts to be formed when H_2S is almost consumed, although experimentally this happens earlier. This might be due to the lack of reactions in the present mechanism describing the interaction between CH_4 and H_2S or to a non appropriate value for the kinetic parameters of the reaction of H_2S with the CH_3OO peroxide, which were estimated to be the same as in the reverse $H_2S + HO_2$ reaction (-R9) by Zhou et al. [11], and mentioned by the authors to be important [19].

5. Conclusions

Oxidation of H_2S at atmospheric pressure has been studied under different reaction atmospheres, varying the air excess ratio (λ) from reducing ($\lambda = 0.32$) to oxidizing conditions ($\lambda = 19.46$). The experiments were carried out in a tubular flow reactor, in the 700–1400 K temperature range and concentrations of H_2S, SO_2 and H_2 were determined. A detailed kinetic mechanism for the conversion of H_2S under the present conditions has been developed, evidencing the importance of given reactions, like the interaction of SH radicals with the radical pool and oxygenated species, such as O_2 and H_2O_2. This mechanism has been used to simulate the experimental results obtained in the present work, together with data from the literature, obtaining a fairly good agreement under the different conditions. The changes in the mechanism included the addition of reaction ($HSOO \rightleftharpoons HSO_2$), supported by recent theoretical works, as a key step in a faster reaction path of SH oxidation, and modification of ($SH + H_2O_2 = H_2S + HO_2$) kinetic parameters, which has a significant impact on the reaction pathways of H_2S oxidation. The main reactions governing the conversion of H_2S have been identified, together with the necessity for a better determination of the kinetic parameters of important reactions, including the isomerization of HSOO into HSO_2 and the interaction of H_2S with HO_2. This work supports the evolution of $SH + O_2$ reaction through HSOO to HSO_2 isomerization.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.proci.2018.05.005.

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