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Experimental and Modeling Investigation of the Effect of H$_2$S Addition to Methane on the Ignition and Oxidation at High Pressures

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Supporting Information

ABSTRACT: The autoignition and oxidation behavior of CH$_4$/H$_2$S mixtures has been studied experimentally in a rapid compression machine (RCM) and a high-pressure flow reactor. The RCM measurements show that the addition of 1% H$_2$S to methane reduces the autoignition delay time by a factor of 2 at pressures ranging from 30 to 80 bar and temperatures from 930 to 1050 K. The flow reactor experiments performed at 50 bar show that, for stoichiometric conditions, a large fraction of H$_2$S is already consumed at 600 K, while temperatures above 750 K are needed to oxidize 10% methane. A detailed chemical kinetic model has been established, describing the oxidation of CH$_4$ and H$_2$S as well as the formation and consumption of organosulfuric species. Computations with the model show good agreement with the ignition measurements, provided that reactions of H$_2$S and SH with peroxides (HO$_2$ and CH$_3$OO) are constrained. A comparison of the flow reactor data to modeling predictions shows satisfactory agreement under stoichiometric conditions, while at very reducing conditions, the model underestimates the contribution of both H$_2$S and CH$_4$. Similar to the RCM experiments, the presence of H$_2$S is predicted to promote oxidation of methane. Analysis of the calculations indicates a significant interaction between the oxidation chemistry of H$_2$S and CH$_4$, but this chemistry is not well understood at present. More work is desirable on the reactions of H$_2$S and SH with peroxides (HO$_2$ and CH$_3$OO) and the formation and consumption of organosulfuric compounds.

INTRODUCTION

The depletion of the traditional natural gas fields and the steadily increasing natural gas consumption have resulted in an increase in the global market share of gases from alternative sources. It is well-known that gases from these sources, such as shale gas, biogas, and so-called sour gas, may contain impurities that affect the combustion behavior of end-use equipment.1 An important “impurity”, present in, for example, sour gases, biogases, and some natural gases, is hydrogen sulfide (H$_2$S). The fraction of H$_2$S in sour gas can exceed several percent.2

The presence of trace amounts of H$_2$S can affect the combustion properties of fuels. Experimental results for fuel/ H$_2$S interactions have been obtained in flow reactors, laminar premixed flames, and shock tubes. Selim et al. investigated the impact of H$_2$S on hydrogen3 and methane4 flames. Flow reactor studies of oxidation of CH$_4$/H$_2$S mixtures have been reported by Arutyunov et al.,5 Chin et al.,6 and Karan and Behie.9 The flame and flow reactor studies are limited to a comparatively low pressure.

Of particular interest in the present work is the effect of H$_2$S on fuel ignition properties at elevated pressure. The impact of H$_2$S on H$_2$10,11 and syngas12 ignition delays has been investigated in shock tubes. Data obtained over a wide range of pressures (1.6–33 atm) and temperatures (1045–1860 K) show that low fractions of H$_2$S in H$_2$/O$_2$ mixtures increase the autoignition delay time, in some cases by a factor of 4 or more compared to neat H$_2$/O$_2$ mixtures.11 In contrast with the behavior of H$_2$/H$_2$S mixtures, modeling studies13 indicate that the presence of H$_2$S reduces the autoignition delay times for methane at high pressures and intermediate temperatures, but no experimental data have been reported.

An improved understanding of the impact of small fractions of H$_2$S on the oxidation characteristics of hydrocarbon fuels is important for combustion equipment, such as homogeneous charge compression ignition (HCCI) engines, where auto-ignition is controlled for optimal performance. Furthermore, the occurrence of autoignition of the fuel/air mixture in spark-ignited gas engines leads to engine knock, which can reduce engine performance and cause engine damage. Understanding the effects of H$_2$S on the autoignition behavior of hydrocarbon fuels is thus essential for quantifying the impact of H$_2$S on the occurrence of knock in engines using natural gas. Moreover, experimental data, such as autoignition delay times and species profiles, are needed to develop and verify detailed chemical mechanisms.

In this paper, we present the results of experiments showing the effects of H$_2$S on methane ignition and oxidation. Autoignition measurements in a rapid compression machine...
(RCM) at pressures ranging from 30 to 80 bar and temperatures from 930 to 1050 K are supplemented by measurements in a laminar flow reactor at 700–900 K and 50 bar. A detailed chemical kinetic model for ignition and oxidation of CH₄/H₂S mixtures is developed, starting from subsets for the oxidation of CH₄, and H₂S as well as the formation and consumption of organosulfuric components, kinetic modeling of the experimental results provides insight into the chemistry of oxidation and serves to evaluate the predictive capability of the model.

## Detailed Kinetic Model

For this study, a chemical kinetic mechanism for the ignition of CH₄/H₂S mixtures has been constructed, with emphasis on reactions important at high pressure. The hydrocarbon subset of the mechanism was drawn from the recent work of Hashemi et al., who studied CH₄ oxidation and ignition at high pressure in a RCM and a flow reactor under conditions similar to those of the present study. This mechanism provides a good prediction of methane oxidation at high pressure over a wide range of conditions.

The H₂S subset was largely drawn from work of Haynes and co-workers. They investigated the chemistry of H₂S pyrolysis and oxidation in a series of modeling studies, supported by ab initio calculations for key reactions. The model of Zhou et al., which was developed to interpret atmospheric pressure flow reactor data, has formed the basis for more recent modeling work on H₂S oxidation, and impact of H₂S on H₂ ignition delays. We have adopted the H₂S subset from the recent study of Song et al., who updated the mechanism of Zhou et al. for application to high pressure.

The interaction between the hydrocarbon and sulfur subsets may involve the formation of methanethiol (CH₃SH) and subsequent conversion of organosulfuric species. Thermodynamic properties and rate constants in this subset were taken mostly from Zheng et al. and van de Vijver et al. Subsets for oxidation of CS₂ and OCS were drawn from previous work by the authors. Selected reactions from the mechanism are listed in Table 1, and the key reactions are discussed in more detail below. The full mechanism is available in the Supporting Information.

Mathieu et al. concluded that a better estimation of several rate constants was needed to improve predictions of H₂/H₂S ignition delays. Their predictions were particularly sensitive to the reaction of H₂S with HO₂ and the SH + SH reaction. The reaction of H₂S with HO₂ has been characterized experimentally at low temperature in both the forward and reverse directions, but only upper limit rate constants have been reported. Zhou calculated the rate constant for the reverse step, SH + H₂O₂ ⇌ H₂S + HO₂ (reaction R1), from theory. Mathieu et al. lowered the Zhou rate constant by a factor of 2 to improve agreement with their experiments. Recent calculations indicate a much lower rate constant, but the level of theory (G3B3 and CBS-QB3) used was lower than that of Zhou. In the present work, we have adopted the value of Mathieu et al. but an accurate determination of this rate constant is desirable.

Because the SH radical is comparatively unreactive toward O₂, its concentration builds up and modeling predictions may become sensitive to the SH + SH reaction. The two major

### Table 1. Selected Reactions for the Hydrocarbon/Sulfur Interaction

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction</th>
<th>A</th>
<th>β</th>
<th>E₀</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ + H₂S → CH₄ + SH</td>
<td>R1</td>
<td>2.8 × 10⁴</td>
<td>2.823</td>
<td>8668</td>
<td>11</td>
</tr>
<tr>
<td>CH₄ + H₂O → H₂ + CH₃OH</td>
<td>R2</td>
<td>3.8 × 10⁴</td>
<td>2.775</td>
<td>−1529</td>
<td>19, 23</td>
</tr>
<tr>
<td>CH₄ + HO₂ → CH₃ + H₂O₂</td>
<td>R3</td>
<td>2.5 × 10⁴</td>
<td>1.477</td>
<td>−2169</td>
<td>19, 23</td>
</tr>
<tr>
<td>CH₄ + O₂ → CH₃ + HO₂ + O</td>
<td>R4</td>
<td>1.5 × 10⁴</td>
<td>2.123</td>
<td>11020</td>
<td>15</td>
</tr>
<tr>
<td>CH₄ + O → CH₃ + O₂</td>
<td>R5</td>
<td>6.8 × 10³</td>
<td>1.200</td>
<td>1434</td>
<td>29</td>
</tr>
<tr>
<td>CH₄ + SH → CH₃SH</td>
<td>R6</td>
<td>7.3 × 10²</td>
<td>0.230</td>
<td>−139</td>
<td>17</td>
</tr>
<tr>
<td>CH₃OO + SH → CH₃O + H₂O</td>
<td>R7</td>
<td>2.5 × 10³</td>
<td>1.477</td>
<td>−2169</td>
<td>b</td>
</tr>
<tr>
<td>CH₃OOH + SH → CH₃OH + H₂O</td>
<td>R8</td>
<td>5.6 × 10²</td>
<td>2.823</td>
<td>8668</td>
<td>c</td>
</tr>
<tr>
<td>CH₃SH + H → CH₃H + S</td>
<td>R9</td>
<td>1.3 × 10³</td>
<td>1.729</td>
<td>986</td>
<td>30</td>
</tr>
<tr>
<td>CH₃SH + H → CH₃ + H₂S</td>
<td>R10</td>
<td>4.1 × 10²</td>
<td>2.925</td>
<td>4750</td>
<td>30</td>
</tr>
<tr>
<td>CH₃SH + H → CH₃ + H₂</td>
<td>R11</td>
<td>7.1 × 10¹</td>
<td>0.766</td>
<td>3220</td>
<td>30</td>
</tr>
<tr>
<td>CH₃SH + H → CH₄ + SH</td>
<td>R12</td>
<td>7.0 × 10¹</td>
<td>1.983</td>
<td>16530</td>
<td>30</td>
</tr>
<tr>
<td>CH₃SH + S → CH₃ + HS</td>
<td>R13</td>
<td>4.2 × 10¹</td>
<td>1.818</td>
<td>80</td>
<td>31, d</td>
</tr>
<tr>
<td>CH₃SH + O → CH₃ + HO</td>
<td>R14</td>
<td>3.3 × 10¹</td>
<td>2.864</td>
<td>1224</td>
<td>31, d</td>
</tr>
<tr>
<td>CH₃SH + OH → CH₃ + H₂O</td>
<td>R15</td>
<td>1.3 × 10¹</td>
<td>1.770</td>
<td>−1689</td>
<td>32</td>
</tr>
<tr>
<td>CH₃SH + OH → CH₃ + H₂O</td>
<td>R16</td>
<td>1.9 × 10¹</td>
<td>2.220</td>
<td>718</td>
<td>32</td>
</tr>
<tr>
<td>CH₃SH + HO₂ → CH₃ + H₂O₂</td>
<td>R17</td>
<td>9.1 × 10⁰</td>
<td>0.000</td>
<td>14300</td>
<td>33</td>
</tr>
<tr>
<td>CH₃SH + HO₂ → CH₃ + H₂O₂</td>
<td>R18</td>
<td>2.0 × 10⁰</td>
<td>0.000</td>
<td>14500</td>
<td>16</td>
</tr>
<tr>
<td>CH₃S + HO₂ → CH₃SH + O₂</td>
<td>R19</td>
<td>1.7 × 10⁻¹</td>
<td>7.490</td>
<td>−12060</td>
<td>34, e</td>
</tr>
<tr>
<td>CH₃S + CH₄ → CH₃ + CH₄</td>
<td>R20</td>
<td>8.1 × 10⁻¹</td>
<td>1.900</td>
<td>1700</td>
<td>16</td>
</tr>
<tr>
<td>CH₃S + CH₃ → CH₃SH + CH₄</td>
<td>R21</td>
<td>1.5 × 10⁻¹</td>
<td>0.000</td>
<td>6500</td>
<td>16</td>
</tr>
<tr>
<td>CH₃S + SH → CH₃ + H₂S</td>
<td>R22</td>
<td>1.2 × 10⁻¹</td>
<td>0.000</td>
<td>5920</td>
<td>17</td>
</tr>
<tr>
<td>CH₃S + H → CH₃S + H</td>
<td>R23</td>
<td>2.5 × 10⁻¹</td>
<td>−8.800</td>
<td>62053</td>
<td>16</td>
</tr>
<tr>
<td>CH₃S + O₂ → CH₃ + SO₂</td>
<td>R24</td>
<td>9.5 × 10⁻²</td>
<td>−3.800</td>
<td>12300</td>
<td>35</td>
</tr>
</tbody>
</table>

Parameters for use in the modified Arrhenius expression k = AT exp[−E/(RT)]. Units are mol, cm, s, and cal. Originally assumed the same as for HO₂ + SH, but the A factor was reduced by a factor of 10 to comply with RCM measurements. Originally assumed the same as for H₂O₂ + SH, but the A factor was reduced by a factor of 10 to comply with RCM measurements. Rate constant fitted in the present work to data reported. From 200 to 800 K.
product channels for this reaction are \( H_2S + S \), which initiates a chain-branching sequence (\( S + O_2 \rightarrow SO + O \), and \( SO + O_2 \rightarrow SO_2 + O \)), and HSSH, which is terminating. We adopted the rate constant for \( H_2S + S \equiv SH + SH \) from Gao et al.,\(^{58}\) while for the \( SH + SH \) recombination reaction, the high-pressure limit from Zhou et al.\(^{25}\) was lowered by a factor of 4, following Song et al.\(^{15}\).

In the recent modeling study of \( CH_4/H_2S \) oxidation by Bongartz and Ghoniem,\(^{19}\) it was assumed that reactions of species containing both carbon and sulfur could be omitted from the reaction mechanism without a significant loss of accuracy. However, the present study indicates that direct interactions between hydrocarbon and sulfur species are important. This chemistry is quite complex. A number of relevant modeling studies have been reported recently in the literature on the pyrolysis of hydrocarbon \( /H_2S \) mixtures\(^ {39,40}\) as well as the pyrolysis\(^ {17} \) and oxidation\(^ {16} \) of hydrocarbon sulfides. Marin and co-workers\(^ {41–45} \) have conducted theoretical studies of the thermodynamics and kinetics of a range of organosulfur compounds, including various thiols and sulfides, and the mechanism of van de Vijver et al.\(^ {17} \) draws on this work.

In the present system, reactions of the \( CH_4 \) radical with the sulfur species pool include
\[
CH_4 + H_2S \equiv CH_4 + SH \\
CH_4 + SH (+M) \equiv CH_3SH (+M)
\]
(R5)
(R6)
The reaction of \( CH_4 \) with \( H_2S \) has been studied experimentally at low to medium temperatures.\(^ {46,47} \) The theoretical studies by Mousavi et al.\(^ {29} \) and very recently Zeng et al.\(^ {48} \) serve to extrapolate the experimental results to higher temperatures. For the recombination of \( CH_4 \) and \( SH \) to form \( CH_3SH \) (reaction \( R6 \)), no measurements are available. An estimate of the second-order rate constant was drawn from the mechanism of van de Vijver et al.\(^ {17} \) but an experimental or theoretical determination of the rate constant for reaction \( R6 \) over a range of pressures and temperatures is desirable.

At the conditions of the present experiments, with high pressure and low to intermediate temperatures, the peroxide chemistry is important for ignition and the interaction of peroxides with sulfur radicals may play a role. We have included in the model the two reactions:
\[
CH_3OO + SH \equiv CH_3O + HSO \\
CH_3OOH + SH \equiv CH_3OO + H_2S
\]
(R7)
(R8)
In the absence of experimental or theoretical data for the two steps, rate constants were initially estimated by analogy with the corresponding reactions of \( HO_2 \) and \( H_2O_2 \) with \( SH \). However, as discussed below, reactions \( R7 \) and \( R8 \) strongly promote ignition and we had to reduce their rate constants by roughly an order of magnitude to avoid a severe underprediction of the ignition delays for \( CH_4/H_2S \) mixtures under RCM conditions.

The rate constants for the reactions of \( CH_3SH \) and its derived radicals (\( CH_3S \) and \( CH_2SH \)) were mostly taken from Zheng et al.\(^ {16} \) and van de Vijver et al.\(^ {17} \). Methanethiol is consumed by \( H \)-abstraction reactions to form mainly \( CH_3S \) (reactions \( R9, R13, R15, \) and \( R17 \)), and the isomer \( CH_2SH \) is only formed in minor amounts (reactions \( R10, R14, R16, \) and \( R18 \)).

The methylthiol radical (\( CH_3S \)) may react with \( O_2 \) (reaction \( R24 \)), the radical pool, or hydrocarbons and organosulfuric species to form larger molecules. For the \( CH_3S + O_2 \) reaction, only room-temperature upper limits are available from the experiment.\(^ {49,50} \) It was studied theoretically by Zhu and Bozzelli.\(^ {35,36} \) At low temperatures, it forms a \( CH_3SOO \) adduct, but with a barrier to dissociation of only \( 10–11 \) kcal mol\(^ {−1} \).\(^ {51,52} \) The adduct has a very limited thermal stability. At higher temperatures, the reaction proceeds to form \( SO_2 \).
\[
CH_3S + O_2 \equiv CH_3 + SO_2
\]
(R24)
We have adopted the rate constant for reaction \( R24 \) calculated by Zhu and Bozzelli.\(^ {35} \)

Flow reactor studies for oxidation of \( CH_4/H_2S \) mixtures under reducing conditions show the formation of \( CS_2 \) and, to a smaller extent, \( OCS \).\(^ {7,8} \) Presently, the conversion of the organosulfuric species to \( CS_2 \) and \( OCS \) is not well established, and this part of the mechanism needs to be revised.

### EXPERIMENTAL SECTION

**RCM.** The autoignition measurements were performed in a RCM, which has been described in detail previously.\(^ {53,54} \) The compositions of the \( CH_4 \) and \( CH_4/H_2S \) (99:1) mixtures studied, expressed as mole percentages, are given in Table 2. The experiments were performed at fuel-lean conditions (fuel/air equivalence ratios of \( \phi = 0.5 \)), and the total concentration of diluting inert gases was close to that of nitrogen in air, while the \( Ar/N_2 \) ratio was chosen to provide temperatures (\( T_c \)) ranging from 930 to 1050 K and pressures (\( P_c \)) from 30 to 80 bar after compression. The gases used in the mixtures all have a purity greater than 99.99%. The pressure in the combustion chamber during compression and throughout the post-compression period was measured using a Kistler ThermoComp quartz pressure sensor with thermal-shock-optimized construction. A creviced piston head\(^ {15} \) was used to preserve a homogeneous reacting core gas during compression and during the post-compression period. The temperature after compression (\( T_p \)) is calculated on the basis of the known composition of the test mixtures, final pressure after compression (\( P_p \)), initial temperature and pressure, and assuming the existence of an adiabatic core.\(^ {25} \) The uncertainty of the calculated core gas temperature (\( T_c \)) is less than \( ±3.5 \) K for all measurements, and the day-to-day reproducibility of the measured autoignition delay time is within 10%.

The autoignition measurements in the RCM have been simulated using the homogeneous reactor software SENSIN,\(^ {55} \) from the CHEMKIN library. To describe the compression and heat loss that occurred during the measurements, the specific volume of the assumed adiabatic core is used as input into the simulations. Because no multi-stage ignition phenomena were observed in the present work, we derive the specific volume directly from the measured pressure trace for the reactive mixture in the period between compression and the moment that substantial heat release begins using the isentropic relations of an ideal gas. Subsequently, we extrapolate the time dependence derived in this fashion to the region in which substantial heat release begins, as described in detail elsewhere.\(^ {53,54} \) Figure 1 shows an example of the measured and simulated pressure profiles.

**Laminar Flow Reactor.** A laboratory-scale high-pressure laminar flow reactor was used to study \( CH_4/H_2S/O_2 \) oxidation at 50 bar and

---

**Table 2. Composition (Mole Fractions) of \( CH_4 \) and \( CH_4/H_2S \) (1% \( H_2S \)) Mixtures Used in the RCM Experiments Presented in Figures 2 and 3**

<table>
<thead>
<tr>
<th>Component</th>
<th>Number 1 (%)</th>
<th>Number 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_4 )</td>
<td>4.76</td>
<td>4.72</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>0</td>
<td>0.052</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>19.05</td>
<td>19.05</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>( \text{Ar} )</td>
<td>46.19</td>
<td>46.18</td>
</tr>
</tbody>
</table>

“The fuel/air equivalence ratio was \( \phi = 0.5 \).”
temperatures up to 900 K. The setup is described in detail elsewhere, and only a brief description is provided here. The reactant gases were premixed before entering the reactor. The reactions took place in a tubular quartz reactor with an inner diameter of 8 mm and a total length of 154.5 cm. For the present operating conditions, the flow reactor was shown by Rasmussen et al. to provide a good approximation to the plug flow. Using a quartz tube and conducting the experiments at high pressure, we expect the contribution from heterogeneous reactions at the reactor wall to be minimized. Our previous work on oxidation of neat CH₄ and H₂S showed no indications of surface effects. The temperature profile in the flow reactor was measured inside the quartz tube. The residence time in the isothermal zone of the reactor was 6.6−10.0 s with the current flow rate of 3.0 NL/min (273 K and 1 atm) and temperatures in the range of 600−900 K. The adiabatic temperature rise as a result of the heat of reaction at full oxidation was calculated to be 22 K. However, as a result of the limited conversion and heat transfer from the hot gas to the surroundings, the actual temperature rise would be considerably lower. All gases used in the experiments were high-purity gases or mixtures with certified concentrations (±2% uncertainty). The product analysis was conducted at the outlet of the reactor by an online 6890N Agilent gas chromatograph (GC-TCD/FID from Agilent Technologies). The relative measuring uncertainty of the GC was in the range of ±6%.

■ RESULTS AND DISCUSSION

Autoignition Delay Times in the RCM. Figure 2 presents the autoignition delay times measured as a function of the temperature $T_c$ at a fixed pressure of $P_c \sim 60$ bar, and in Figure 3, measurements are presented at a fixed temperature of $T_c \sim 970 \pm 3.5$ K for pressures ranging from $P_c \sim 30$ to 80 bar (see Table 2 for the compositions used). The results show that the addition of 1% H₂S to methane decreases the autoignition delay time by about a factor of 2 for all temperatures and pressures measured. The promoting effect of H₂S on oxidation is in agreement with the flow reactor results described below. In contrast, the addition of low fractions of H₂S to hydrogen was seen to result in a substantial increase in the autoignition delay time at pressures around 33 bar and temperatures higher than 1190 K, while at lower temperatures, H₂S addition to hydrogen was seen to reduce the delay time only slightly compared to pure H₂.

Figures 2 and 3 compare the autoignition measurements to the predicted ignition delay times. The calculated and observed autoignition delay times for pure CH₄ and the CH₄/H₂S mixtures are in good agreement for the measured pressures and temperatures.

To analyze the effect of H₂S on ignition under these experimental conditions, reaction path and sensitivity analyses were conducted. The results shown in Figures 4 and 5 have been performed for 80 bar and 970 K. The sensitivity coefficients are obtained using

$$S_{\tau/k} = \frac{(\Delta \tau/\tau)}{(\Delta k/k)}$$

(1)

A positive sensitivity coefficient $S_{\tau}$ indicates that an increase in the reaction rate constant leads to an increase in the predicted autoignition delay time. The sensitivity analysis shows that the predicted autoignition delay time is strongly sensitive to the reaction of methane with the radicals OH and HO₂:

$$CH_4 + OH \rightleftharpoons CH_3 + H_2O$$

$$CH_4 + HO_2 \rightleftharpoons CH_3 + H_2O_2$$

and to the fate of the relatively unreactive methyl radicals. At the high pressure, the peroxide chemistry becomes important for the predicted ignition delay as discussed in detail by...
Hashemi et al. The formation of HO$_2$ and H$_2$O$_2$ as well as CH$_3$OO and CH$_3$OOH plays an important role in the oxidation of both methane and the methyl radical. The methyl radical is converted to CH$_2$O directly by reaction with O$_2$ and indirectly via CH$_3$ $\rightarrow$ CH$_2$O $\rightarrow$ CH$_3$OO $\rightarrow$ CH$_2$O, H$_2$O $\rightarrow$ CH$_3$OOH $\rightarrow$ CH$_2$O $\rightarrow$ CH$_3$O, and CH$_3$ $\rightarrow$ CH$_3$OO $\rightarrow$ CH$_3$O $\rightarrow$ CH$_2$O. Hydrogen peroxide, formed from H-abstraction reactions of HO$_2$, yields OH radicals via thermal dissociation, H$_2$O$_2$ (+M) $\rightarrow$ OH + OH (+M), further promoting oxidation of methane.

When H$_2$S is added to methane, reactions between H$_2$S and peroxides and between methyl peroxide and SH become competitive with reactions in the methane oxidation subset and serve to promote ignition.

$$H_2S + HO_2 \rightarrow SH + H_2O_2$$

$$H_2S + CH_3OO \rightarrow SH + CH_3OOH$$  (R8b)

$$CH_3OO + SH \rightarrow CH_3O + HSO$$

The modeling predictions appear to support the value of $k_1$ proposed by Mathieu et al. but rate constants for several of the key sulfur reactions are uncertain. To obtain an acceptable agreement between predictions and experiment, we found it necessary to decrease the rate constants for reactions R7 and R8 by an order of magnitude compared to the values calculated by Zhou for the similar reactions of HO$_2$.

The reaction path and sensitivity analyses presented in Figures 4 and 5 indicate that the addition of H$_2$S to methane has an impact on both the O/H radical pool and the hydrocarbon oxidation channels. The interaction between H$_2$S and the H$_2$/O$_2$ subset plays an important role in the formation of chain carriers in the early stage of the ignition process. The rapid formation of OH radicals in the early stage, mainly through the sequence H$_2$S + HO$_2$ $\rightarrow$ SH + H$_2$O$_2$ (reaction R1b), H$_2$O$_2$ (+M) $\rightarrow$ OH + OH (+M), SH + HO$_2$ $\rightarrow$ HSO + OH (reaction R3), enhances the ignition process. Ignition is further promoted by reaction of H$_2$S (reaction R8b) and SH (reaction R7) with the CH$_3$OO radical, while recombination of CH$_3$ and SH (reaction R6), feeding into
the organosulfuric species pool, and \( \text{SH} + \text{HO}_2 \rightarrow \text{H}_2\text{S} + \text{O}_2 \) (reaction R2) are chain-terminating.

**Oxidation in the Flow Reactor.** The flow reactor experiments were conducted at 50 bar and fuel/air equivalence ratios of \( \phi = 22.8 \) (\( \text{H}_2\text{S}/\text{CH}_4 \sim 1.6\% \)) and \( \phi = 1.1 \) (\( \text{H}_2\text{S}/\text{CH}_4 \sim 14\% \)). Figures 6 and 7 compare measured and predicted species fractions in the outlet of the reactor versus the reactor temperature. For the fuel-rich mixture, the onset of \( \text{H}_2\text{S} \) oxidation (10% conversion) is around 650 K. At this temperature, roughly 6% oxygen is consumed and the major product is SO\(_2\). Above 750 K, \( \text{H}_2\text{S} \) is completely consumed. Sulfur dioxide remains the major product, even at higher temperatures, because methane conversion is very limited under these conditions.

For the stoichiometric mixture, about 40% \( \text{H}_2\text{S} \) has been consumed already at 600 K, where \( \text{CH}_4 \) is largely unreacted. A 10% conversion of oxygen is achieved at 725 K, while a temperature of 775 K is needed to oxidize 10% methane. Similar to fuel-rich conditions, the methane conversion is limited; therefore, the major product is SO\(_2\). The sulfur and carbon balances close within 8 and 2%, respectively, throughout the experiments. For the fuel-rich case, however, a considerable amount of oxygen (up to 28%) is not taken into account; presumably this difference is due to formation of unmeasured oxygenated products.

Under very fuel-rich conditions (Figure 6), the model severely underpredicts the observed conversion of both \( \text{H}_2\text{S} \) and \( \text{CH}_4 \). Under stoichiometric conditions (Figure 7), predictions are in better agreement with the measurements. The major difference is that the model predicts the onset of \( \text{H}_2\text{S} \) conversion to occur at 700 K, while the experimental data indicate \( \text{H}_2\text{S} \) oxidation even below 600 K. The onset of the reaction for \( \text{CH}_4 \) and \( \text{O}_2 \) at around 725 K is captured well by the model, while above 750 K, the consumption of these reactants is slightly overpredicted, resulting in overprediction of the concentrations of \( \text{C}_2\text{H}_4, \text{CO} \), and \( \text{CO}_2 \). Comparisons to simulations for undoped mixtures of \( \text{CH}_4/\text{O}_2 \) (data not shown) indicate a promoting effect of \( \text{H}_2\text{S} \) on methane oxidation,
similar to what was observed in the RCM experiments. The predicted methane conversion is negligible at temperatures below 850 K for neat mixtures of CH₄/O₂ (both stoichiometries), while for mixtures of CH₄/O₂/H₂S, the temperature for the onset of the reaction is calculated to be about 700 K.

As shown in the reaction pathway diagram for CH₄/H₂S oxidation (Figure 4), oxidation pathways for the flow reactor conditions are similar to those predicted for the RCM. However, the results must be interpreted cautiously as a result of the discrepancies between modeling predictions and experimental data. Figure 8 shows the sensitivity of the model predictions toward reaction rate constants for both stoichiometries at 725 K.

According to the model, the reaction H₂S + O₂ → SH + HO₂ initiates the H₂S oxidation. The fate of the SH radical is important for the oxidation of both CH₄ and H₂S. Predictions are particularly sensitive to the branching fraction of the SH + HO₂ reaction between HSO + OH (reaction R3, chain propagating) and H₂S + O₂ (reaction R2, terminating). Also the reactions SH + O₂ → SO₂ + H (reaction R4) and SH + SH → H₂S + S promote oxidation, while recombination of SH with CH₄ (reaction R6) inhibits reaction. In line with findings for high-pressure oxidation of neat methane, reactions involving the CH₃OO radical are rate-controlling for the CH₄/H₂S mixture. Similar to the RCM conditions, reactions of H₂S (reaction R8b) and SH (reaction R7) with the CH₃OO radical strongly promote oxidation.

**SUMMARY AND CONCLUSION**

The autoignition and oxidation behavior of CH₄/H₂S mixtures have been studied experimentally in a RCM and flow reactor. The results were interpreted in terms of a detailed chemical kinetic model, describing the oxidation of CH₄ and H₂S as well as the formation and consumption of organosulfuric species. Autoignition measurements performed in a RCM at pressures of 30–80 bar and temperatures from 930 to 1050 K show that the addition of 1% H₂S to methane reduces the autoignition delay time by a factor of 2 compared to neat methane. Predictions with the model agree well with the measured autoignition delay times, provided that reactions of H₂S and SH with peroxides (HO₂ and CH₃OO) are constrained.

In the flow reactor at 50 bar and temperatures of 600–900 K, a large part of H₂S is consumed already at 600 K, while temperatures around 775 K are needed to oxidize 10% methane. Similar to the RCM results, H₂S has a promoting effect on the oxidation of methane. A comparison of the flow reactor data to modeling predictions shows satisfactory agreement under stoichiometric conditions, while at very reducing conditions, the model underestimates the consumption of both H₂S and CH₄. Our work indicates that the H₂S oxidation chemistry and the interaction of CH₄ and H₂S at high pressure are not well understood. More work is desirable on the reactions of H₂S and SH with peroxides (HO₂ and CH₃OO) and the formation and consumption of organosulfuric compounds.

**ASSOCIATED CONTENT**

* Supporting Information
  
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.6b02140.

  Full mechanism (TXT)

  Thermodynamic properties (TXT)

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**Notes**

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