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Experimental and Modeling Investigation of the Effect of H₂S Addition to Methane on the Ignition and Oxidation at High Pressures

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Supporting Information

ABSTRACT: The autoignition and oxidation behavior of CH₄/H₂S 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% H₂S 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 H₂S 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 CH₄ and H₂S 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 H₂S and SH with peroxides (HO₂ and CH₃OO) 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 consumption of both H₂S and CH₄. Similar to the RCM experiments, the presence of H₂S is predicted to promote oxidation of methane. Analysis of the calculations indicates a significant interaction between the oxidation chemistry of H₂S and CH₄, but this chemistry is not well understood at present. More work is desirable on the reactions of H₂S and SH with peroxides (HO₂ and CH₃OO) 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 (H₂S). The fraction of H₂S in sour gas can exceed several percent.²

The presence of trace amounts of H₂S can affect the combustion properties of fuels. Experimental results for fuel/H₂S interactions have been obtained in flow reactors, laminar premixed flames, and shock tubes. Selim et al. investigated the impact of H₂S on hydrogen³⁴ and methane⁵⁶ flames. Flow reactor studies of oxidation of CH₄/H₂S mixtures have been reported by Arutyunov et al.,⁷ Chin et al.,⁸ and Karan and Belic.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 H₂S on fuel ignition properties at elevated pressure. The impact of H₂S on H₂¹⁰¹¹ 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 H₂S in H₂/O₂ mixtures increase the autoignition delay time, in some cases by a factor of 4 or more compared to neat H₂/O₂ mixtures.¹¹ In contrast with the behavior of H₂/H₂S mixtures, modeling studies¹³ indicate that the presence of H₂S 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 H₂S on the oxidation characteristics of hydrocarbon fuels is important for combustion equipment, such as homogeneous charge compression ignition (HCCI) engines, where autoignition 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 H₂S on the autoignition behavior of hydrocarbon fuels is thus essential for quantifying the impact of H₂S 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 H₂S on methane ignition and oxidation. Autoignition measurements in a rapid compression machine...
We have adopted the H$_2$S subset from the formation and consumption of organosulfuric components. We have adopted the H$_2$S subset from the formation and consumption of organosulfuric components. By and oxidation in a series of modeling studies, supported recent study of Song et al., who updated the mechanism of 200 to 800 K.

For this study, a chemical kinetic mechanism for the ignition of CH$_4$/H$_2$S mixtures has been constructed, with emphasis on reactions important at high pressure. The hydrocarbon subset of the mechanism was drawn from previous work by van de Vijver et al. Subsets for oxidation of CS$_2$ 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 H$_2$/H$_2$S ignition delays. Their predictions were particularly sensitive to the rate constant for the reverse step, SH + H$_2$O$_2$ → H$_2$S + OH. Zhou et al. lowered the level of theory (G3B3 and CBS-QB3) used in the present work to data reported. From 200 to 800 K.

The interaction between the hydrocarbon and sulfur subsets may involve the formation of methanethiol (CH$_3$SH) 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 CS$_2$ 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.

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product channels for this reaction are H₂S + S, which initiates a chain-branching sequence (S + O₂ → SO + O, and SO + O₂ → SO₂ + O), and HSSH, which is terminating. We adopted the rate constant for H₂S + S ⇌ SH + SH from Gao et al., while for the SH + SH recombination reaction, the high-pressure limit from Zhou et al. was lowered by a factor of 4, following Song et al. 

In the recent modeling study of CH₄/H₂S oxidation by Bongartz and Ghoniem, 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/H₂S mixtures as well as the pyrolysis and oxidation of hydrocarbon sulfides. Marin and co-workers 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. draws on this work. In the present system, reactions of the CH₃ radical with the sulfur species pool include

\[
\text{CH}_3 + \text{H}_2\text{S} \rightleftharpoons \text{CH}_4 + \text{SH} \tag{R5}
\]

\[
\text{CH}_3 + \text{SH} \rightleftharpoons \text{CH}_2\text{SH} \tag{R6}
\]

The reaction of CH₃ with H₂S has been studied experimentally at low to medium temperatures. The theoretical studies by Mousavipour et al. and very recently Zeng et al. serve to extrapolate the experimental results to higher temperatures. For the recombination of CH₃ and SH to form CH₃SH (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., 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.

\[
\text{CH}_3\text{OO} + \text{SH} \rightleftharpoons \text{CH}_2\text{O} + \text{HSO} \tag{R7}
\]

\[
\text{CH}_3\text{OOH} + \text{SH} \rightleftharpoons \text{CH}_2\text{O} + \text{H}_2\text{S} \tag{R8}
\]

In the absence of experimental or theoretical data for the two steps, rate constants were initially estimated by analogy with the corresponding reactions of HO₂ and H₂O₂ 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 CH₄/H₂S mixtures under RCM conditions.

The rate constants for the reactions of CH₃SH and its derived radicals (CH₃S and CH₂SH) were mostly taken from Zheng et al. and van de Vrijer et al. Methanethiol is consumed by H-abstraction reactions to form mainly CH₃S (reactions R9, R13, R15, and R17), and the isomer CH₂SH is only formed in minor amounts (reactions R10, R14, R16, and R18).

The methylthyl radical (CH₃S) may react with O₂ (reaction R24), the radical pool, or hydrocarbons and organosulfuric species to form larger molecules. For the CH₃S + O₂ reaction, only room-temperature upper limits are available from the experiment. It was studied theoretically by Zhu and Bozzelli. At low temperatures, it forms a CH₂SOO adduct, but with a barrier to dissociation of only 10–11 kcal mol⁻¹, the adduct has a very limited thermal stability. At higher temperatures, the reaction proceeds to form SO₂.

\[
\text{CH}_3\text{S} + \text{O}_2 \rightleftharpoons \text{CH}_4 + \text{SO}_2 \tag{R24}
\]

We have adopted the rate constant for reaction R24 calculated by Zhu and Bozzelli. Flow reactor studies for oxidation of CH₄/H₂S mixtures under reducing conditions show the formation of CS₂ and, to a smaller extent, OCS. Presently, the conversion of the organosulfuric species to CS₂ 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. The compositions of the CH₄ and CH₄/H₂S (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 φ = 0.5), and the total concentration of diluting inert gases was close to that of nitrogen in air, while the Ar/N₂ ratio was chosen to provide temperatures (Tc) ranging from 930 to 1050 K and pressures (Pc) 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 was used to preserve a homogeneous reacting core gas during compression and during the post-compression period. The temperature after compression (Tc) is calculated on the basis of the known composition of the test mixtures, final pressure after compression (Pc), initial temperature and pressure, and assuming the existence of an adiabatic core. The uncertainty of the calculated core gas temperature (Tc) 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 SENKIN 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. 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 CH₄/H₂S/O₂ oxidation at 50 bar and...
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 ($\pm$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 $\pm$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

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

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:

$$\text{CH}_4 + \text{OH} \rightleftharpoons \text{CH}_3 + \text{H}_2\text{O}$$

$$\text{CH}_4 + \text{HO}_2 \rightleftharpoons \text{CH}_3 + \text{H}_2\text{O}_2$$

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
The formation of HO₂ and H₂O₂ as well as CH₃OO and CH₃OOH plays an important role in the oxidation of both methane and the methyl radical. The methyl radical is converted to CH₂O directly by reaction with O₂ and indirectly via CH₃ → CH₂O → CH₃O, CH₃ → CH₃OO → CH₃OOH → CH₂O → CH₂O, and CH₃ → CH₂OOH → CH₂O → CH₂O. Hydrogen peroxide, formed from H-abstraction reactions of HO₂, yields OH radicals via thermal dissociation, H₂O₂ (+M) → OH + OH (+M), further promoting oxidation of methane.

When H₂S is added to methane, reactions between H₂S and peroxides and between methyl peroxide and SH become competitive with reactions in the methane oxidation subset and serve to promote ignition.

\[ \text{H}_2\text{S} + \text{HO}_2 \rightarrow \text{SH} + \text{H}_2\text{O}_2 \]  
\[ \text{H}_2\text{S} + \text{CH}_3\text{OO} \rightarrow \text{SH} + \text{CH}_3\text{OOH} \]  
\[ \text{CH}_3\text{OO} + \text{SH} \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \] (R8b)

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 HO₂.

The reaction path and sensitivity analyses presented in Figures 4 and 5 indicate that the addition of H₂S to methane has an impact on both the O/H radical pool and the hydrocarbon oxidation channels. The interaction between H₂S and the H₂/O₂ 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 H₂S + HO₂ → SH + H₂O₂ (reaction R1b), H₂O₂ (±M) → OH + OH (±M), SH + H₂O₂ = HSO + OH (reaction R3), enhances the ignition process. Ignition is further promoted by reaction of H₂S (reaction R8b) and SH (reaction R7) with the CH₃OO radical, while recombination of CH₃ 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 \( \phi = 22.8 \) (H\(_2\)S/CH\(_4\) \( \sim \) 1.6%) and \( \phi = 1.1 \) (H\(_2\)S/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 H\(_2\)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, H\(_2\)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% H\(_2\)S has been consumed already at 600 K, where 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 H\(_2\)S and 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 H\(_2\)S conversion to occur at 700 K, while the experimental data indicate H\(_2\)S oxidation even below 600 K. The onset of the reaction for CH\(_4\) and 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 C\(_2\)H\(_6\), CO, and CO\(_2\). Comparisons to simulations for undoped mixtures of CH\(_4\)/O\(_2\) (data not shown) indicate a promoting effect of H\(_2\)S on methane oxidation.

**Figure 6.** Results of experiments with CH\(_4\)/H\(_2\)S in the flow reactor at 50 bar. Inlet composition: 1.25% CH\(_4\), 1110 ppm of O\(_2\), 200 ppm of H\(_2\)S, and balance N\(_2\) (\( \phi = 22.8 \)). The gas residence time is calculated as \( \tau \) (s) = \( 5990/T \) (K).

**Figure 7.** Results of experiments with CH\(_4\)/H\(_2\)S in the flow reactor at 50 bar. Inlet composition: 1500 ppm of CH\(_4\), 3010 ppm of O\(_2\), 200 ppm of H\(_2\)S, and balance N\(_2\) (\( \phi = 1.1 \)). The gas residence time is calculated as \( \tau \) (s) = \( 5920/T \) (K).
similar to what was observed in the RCM experiments. The predicted methane conversion is negligible at temperatures below 850 K for neat mixtures of CH\textsubscript{4}/O\textsubscript{2} (both stoichiometries), while for mixtures of CH\textsubscript{4}/O\textsubscript{2}/H\textsubscript{2}S, the temperature for the onset of reaction is calculated to be about 700 K. As shown in the reaction pathway diagram for CH\textsubscript{4}/H\textsubscript{2}S 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 H\textsubscript{2}S + O\textsubscript{2} = SH + HO\textsubscript{2} initiates the H\textsubscript{2}S oxidation. The fate of the SH radical is important for the oxidation of both CH\textsubscript{4} and H\textsubscript{2}S. Predictions are particularly sensitive to the branching fraction of the SH + HO\textsubscript{2} reaction between HSO + OH (reaction R3, chain propagating) and H\textsubscript{2}S + O\textsubscript{2} (reaction R2, terminating). Also the reactions SH + O\textsubscript{2} → SO\textsubscript{2} + H (reaction R4) and SH + SH → H\textsubscript{2}S + S promote oxidation, while recombination of SH with CH\textsubscript{3} (reaction R6) inhibits reaction. In line with findings for high-pressure oxidation of neat methane\textsuperscript{14}, reactions involving the CH\textsubscript{3}OO radical are rate-controlling for the CH\textsubscript{4}/H\textsubscript{2}S mixture. Similar to the RCM conditions, reactions of H\textsubscript{2}S (reaction R8b) and SH (reaction R7) with the CH\textsubscript{3}OO radical strongly promote oxidation.

**SUMMARY AND CONCLUSION**

The autoignition and oxidation behavior of CH\textsubscript{4}/H\textsubscript{2}S 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 CH\textsubscript{4} and H\textsubscript{2}S 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% H\textsubscript{2}S 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 H\textsubscript{2}S and SH with peroxides (HO\textsubscript{2} and CH\textsubscript{3}OO) are constrained.

In the flow reactor at 50 bar and temperatures of 600−900 K, a large part of H\textsubscript{2}S is consumed already at 600 K, while temperatures around 775 K are needed to oxidize 10% methane. Similar to the RCM results, H\textsubscript{2}S 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 H\textsubscript{2}S and CH\textsubscript{4}. Our work indicates that the H\textsubscript{2}S oxidation chemistry and the interaction of CH\textsubscript{4} and H\textsubscript{2}S at high pressure are not well understood. More work is desirable on the reactions of H\textsubscript{2}S and SH with peroxides (HO\textsubscript{2} and CH\textsubscript{3}OO) 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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