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# Shock-tube water time-histories and ignition delay time measurements for H<sub>2</sub>S near atmospheric pressure

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## Abstract

Hydrogen sulfide combustion has been of interest in recent years due to its presence in coal-derived syngas and in sour gas. However, there are limited data available for the calibration of chemical kinetics models of high-temperature H<sub>2</sub>S oxidation. Ignition delay times and laser-absorption water time histories were therefore measured in two different shock tubes around atmospheric pressure over a range of temperatures from 1445 to 2210 K for H<sub>2</sub>S-O<sub>2</sub> mixtures diluted in 98% Ar. While modern H<sub>2</sub>S models from the literature predicted the ignition delay times with fair accuracy, the water profiles were initially very poorly predicted with the same kinetic mechanisms. A model analysis showed that the reaction R62, SH + HO<sub>2</sub> ⇌ H<sub>2</sub>S + O<sub>2</sub> (in reverse), was chiefly responsible for these poor predictions. It was possible to obtain better water predictions when the rate for R62 was divided by 10. A tentative model is proposed herein, based on this assumption for R62, and good predictions were obtained for both the ignition delay times and water profiles, as well as for former high-pressure shock-tube data with H<sub>2</sub>-H<sub>2</sub>S mixtures. The present study shows that more accurate rates for the reactions R62 (SH + HO<sub>2</sub> ⇌ H<sub>2</sub>S + O<sub>2</sub>), R75 (SH + O<sub>2</sub> ⇌ HSO + O), and R46 (SH + SH (+M) ⇌ HSSH (+M)) would be needed to better predict H<sub>2</sub>S combustion chemistry.

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*Keywords:* Shock tube; H<sub>2</sub>S; Ignition delay time; Water; Laser absorption

## 1. Introduction

Hydrogen sulfide (H<sub>2</sub>S) is an important and regulated by-product of the oil industry and also a constituent (up to 30% by vol.) of a large fraction of natural gas resources (so-called sour natural gas) [1]. Syngas blends produced from either coal

or biomass can also contain H<sub>2</sub>S, up to 1.3% mol [2], and it has been shown that H<sub>2</sub>S, even in small proportion, can have a noticeable effect on important combustion properties such as ignition delay time ( $\tau_{\text{ign}}$ ) [2,3] and flame speed [4] for hydrogen-based mixtures. For these reasons, H<sub>2</sub>S combustion chemistry has been the topic of several recent studies [1,3,5–9].

However, despite these recent studies, the combustion chemistry of H<sub>2</sub>S is still not very well understood. This lack of understanding is due to both the very limited amount of experimental data

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available to validate the models and to the presence of many sensitive reactions with a relatively high uncertainty in the models [1,3,7]. In addition, some of the few experimental data available seem to suffer from large uncertainties. For instance, a difference as large as 20 cm/s can be observed between laminar burning velocity studies of H<sub>2</sub>S at stoichiometric, room conditions [1]. The effects of surface reactions in quartz flow reactors are also unclear and, even with surface coating to prevent catalytic reactions, Zhou et al. [7] were not able to model all of their experiments without changing a few reaction rates from one condition to the other.

The model from Zhou et al. [7], owing to its larger number of species/reactions and to the fact that numerous important reactions have been determined by high-level calculation, has been recently used as a foundation for several studies aiming to improve H<sub>2</sub>S combustion chemistry [1,3,9]. Mathieu et al. [3] measured ignition delay times of diluted mixtures of H<sub>2</sub>/O<sub>2</sub> seeded with various amount of H<sub>2</sub>S between 1.5 and 35 atm. Using their data as a support, they changed a few reaction rates from the Zhou et al. mechanism within their uncertainties and were able to reproduce their ignition delay time data and some other data from the literature. However, they failed to reproduce the flow reactor data from Zhou et al. [7]. More recently, Bongartz and Ghoniem [1] also started from the Zhou et al. mechanism and tried to optimize H<sub>2</sub>S chemistry by using several targets, including laminar burning velocities and flow reactor results from Zhou et al. [7]. They identified that it was necessary to change the rates of 15 reactions within their uncertainties; good agreement was found between the model and the data when optimizing against laminar burning velocity, ignition delay time, and pyrolysis data (“Optimization 1–7” in their paper) or for the flow reactor data of Zhou and coworkers. Larger discrepancies were observed for a combination of all these data as targets (“Optimization 1–12”). They also observed that the rates of several important reactions were changed in opposite directions in the optimization method, depending on which targets were used. They concluded that more accurate direct determinations of the rate constant were needed for these important reactions, without pointing at a particular reaction.

The present study was initiated to improve H<sub>2</sub>S combustion chemistry by presenting new ignition delay time ( $\tau_{\text{ign}}$ ) and water time-history profiles in shock tubes for H<sub>2</sub>S/O<sub>2</sub> mixtures in 98% Ar around atmospheric pressure and for 3 equivalence ratios ( $\phi$ ): 0.5, 1.0, and 1.5. Using these results as a guide, a tentative H<sub>2</sub>S kinetics mechanism is proposed herein. Details on the experimental procedure are covered first, followed by the experimental results and the model’s improvements and validation stages.

## 2. Experimental apparatuses

Laser absorption and ignition delay time experiments were conducted in two different shock tubes. Although the dimensions of these facilities are slightly different, they share some similarities, described below. Both tubes are single-diaphragm, made of stainless-steel, with a 7.62-cm i.d. driver section (2.46-m long for the ignition delay time tube (IST); 3-m long for the water diagnostic tube (DST)) with a large-diameter driven section (15.24-cm i.d., 4.72-m long for the IST; 16.2-cm i.d., 6.78-m long for the DST). In both cases, PCB P113A piezoelectric pressure transducers were used along the driven section to measure the incident-wave velocities. A curve fit of the measured velocities was used to determine the incident wave speed at the endwall location. Post reflected-shock conditions were obtained using this extrapolated wave speed in conjunction with the one-dimensional shock relations and the initial conditions in the test region. This method was proven to maintain the uncertainty in the temperature determination behind reflected shock waves ( $T_5$ ) below 10 K as described in Petersen et al. [10]. Test pressure was monitored by a Kistler 603 B1 transducer located at the sidewall, in the same plane as the observation windows (sapphire, 16 mm from the endwall). Non-ideal boundary layer effects measured by the change in pressure ( $dP/dt$ ) behind the reflected shock wave were determined to be less than 2%/ms in each facility. Polycarbonate diaphragms (0.25-mm thickness) were used, and a cross-shaped cutter was employed to facilitate their breakage and prevent fragments from tearing off. The driven sections were vacuumed down to  $2 \times 10^{-5}$  Torr or better prior to every run. The pumping time between experiments was minimized using a pneumatically driven poppet valve matching the inside diameter of the driven section for each tube. Test mixtures were prepared manometrically in a stainless steel mixing tank shared by the two facilities.

The gases, O<sub>2</sub>, Ar (both 99.999% purity), and H<sub>2</sub>S (1.01% H<sub>2</sub>S (99.9% purity) diluted in Ar (99.999%) by Praxair) were passed through a perforated tube traversing the center of the mixing vessel to allow for rapid, turbulent mixing. The conditions investigated and experimental results ( $\tau_{\text{ign}}$  and water profiles, along with corresponding pressure and temperature conditions behind the reflected shock waves (RSW)) are provided as supplementary material.

### 2.1. Ignition delay time shock tube

Ignition delay time was defined as the time between the passage of the RSW and the intersection of lines drawn along the steepest rate-of-change of OH\* de-excitation (i.e., chemiluminescence) and a horizontal line which defines the

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