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Effects of organic silicon compounds on syngas auto-ignition behavior

Rachel A. Schwind*, Margaret S. Wooldridge

Department of Mechanical Engineering, University of Michigan, Ann Arbor, 2350 Hayward Street, Ann Arbor, MI 48109, United States

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ABSTRACT

Siloxanes are a significant impurity in syngas feedstocks and an important source of silicon in combustion synthesis applications. However, little is known regarding the fundamental combustion chemistry of siloxane compounds. The impact of two organic silicon species with different but related chemical structures, trimethylsilanol (TMSO) and hexamethyldisiloxane (HMDSO), on syngas auto-ignition behavior was investigated in this study using physical and computational experiments. A rapid compression facility (RCF) was used to create temperatures of 1010–1070 K and pressures of 8–10.3 atm for auto-ignition experiments. Experiments with trace concentrations of TMSO (100 ppm, mole basis) or HMDSO (100 ppm) were added to a surrogate syngas blend (CO and H_2 with a molar ratio of 2.34:1, air levels of dilution, with molar equivalence ratios of $\phi = 0.1$). The measured ignition delay times showed both siloxane species promote ignition behavior with TMSO yielding faster ignition delay times by approximately 37% and HMDSO yielding faster times by approximately 50% compared with the reference syngas mixture which contained no siloxanes. A computational study was conducted to interpret the results of the ignition experiments. Because detailed chemistry does not exist for these organo-silicon compounds, the effects of the addition of CH_3, H, and OH radicals to H_2 and CO mixtures were explored to simulate the potential rapid decomposition of the siloxanes in the H_2 and CO system. Addition of the radicals decreased the predicted ignition delay times when compared with the H_2 and CO mixture simulations without the radical species, but the simulations did not fully capture the behavior observed in the experiments, indicating the siloxane chemistry is more complex than providing a rapid source of radicals.

1. Introduction

Interest in syngas combustion applications has been growing as energy technologies move from fossil fuels to rely more on sustainable and renewable fuels. In particular, syngas derived from second generation feed stocks such as landfill gas and sewage gas is an important pathway to mitigate environmental impacts of landfills and wastewater treatment plants while simultaneously displacing fossil fuels. Currently landfill gas is under-utilized with less than a quarter of landfills reporting capture of the methane rich gas emissions as of 2016 [1].

The different sources for syngas production are introducing compounds that have not previously been present into biogas and syngas mixtures, like siloxanes. Siloxanes have become increasingly prevalent in industrial products and processes (e.g., shampoos, creams, food production, oil, etc.) and are making their way into landfills and wastewater and thus into the landfill gas emissions and biogas produced from landfills and sewage gas [2,3]. Siloxanes present even at low concentrations in syngas can have dramatic impact on combustion applications, for example the nanoparticulate SiO_2 particles formed as a product of combustion can lead to significant fouling of surfaces found in heat exchangers and other appliances [3,4] and can cause abrasive damage in reciprocating engines [2,5,6].

The most common organic silicon compounds found in gas derived from landfills are octamethylcyclotetrasiloxane (OMCTSO), hexamethyldisiloxane (HMDSO), and trimethylsilanol (TMSO) [2,7]. Little is known about the combustion chemistry of these organic silicon compounds. The only combustion studies to date of TMSO are by Mansfield and Wooldridge [8] and of HMDSO by Feroughi et al. [9] and Chrystie et al. [10]. Mansfield and Wooldridge [8] conducted experimental studies of auto-ignition of syngas mixtures of H_2 and CO including the impact of trace amounts (10 ppm and 100 ppm, mole basis) of TMSO at 5 and 15 atm for a range of temperatures from ~1010–1110 K. The results showed notable impact from the addition of TMSO where the reactivity of the mixtures increased dramatically. The TMSO also affected the pressure dependence of the H_2 and CO mixtures. While Mansfield and Wooldridge [8] conjectured on the reaction pathways of TMSO leading to the observed behavior, the detailed kinetics were not identified. Feroughi et al. [9] studied synthesis of silicon

* Corresponding author.
E-mail address: schwinra@umich.edu (R.A. Schwind).

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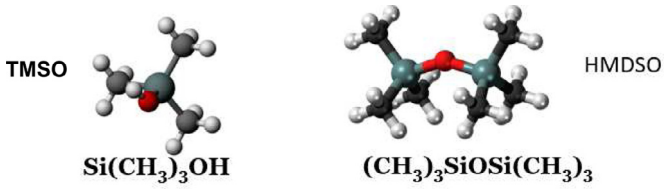

Fig. 1. Molecular structures of siloxanes studied in the current work: trimethylsilanol (TMSO) and hexamethyldisiloxane (HMDSO).

dioxide nanoparticles in a hydrogen/oxygen laminar premixed flame seeded with small amounts (200 ppm) of HMDSO. A global reaction for HMDSO + OH was proposed and integrated into a detailed reaction mechanism for silane (SiH_4), but the approximation of the global reaction was identified as a source of uncertainty and possible discrepancy between the model predictions and the experimental observations.

The objective of the current study was to provide new qualitative and quantitative understanding of the combustion chemistry of siloxanes in order to better anticipate and control their effects on combustion applications. The new experimental data on HMDSO ignition were compared with results on TMSO ignition to understand the effects of siloxane chemical structure. The technical approach used auto-ignition experiments to explore the effects of trace amounts of different siloxane compounds on the auto-ignition behavior of syngas (H_2 and CO) mixtures. Both existing ignition data on TMSO and new data were used for the comparison with HMDSO.

The chemical structures of TMSO and HMDSO are presented in Fig. 1. Both compounds are directly relevant to biogas with siloxane impurities and comparison of the two species also emphasizes the effect of doubling the $Si(CH_3)_3$ structural contribution to the combustion chemistry. The results are interpreted in the context of possible reaction pathways leading to the observed ignition behaviors.

2. Methods

2.1. Ignition experiments

The ignition behavior was studied utilizing the University of Michigan rapid compression facility (RCF). Three fuel mixtures were used: (1) H_2 and CO with a molar ratio of CO:H_2 = 2.34:1, (2) the same base mixture of H_2 and CO with 0.25% HMDSO (mole fraction basis of the total fuel), and (3) the base mixture of H_2 and CO with 0.25% TMSO (mole fraction basis of the total fuel). Each mixture had a fuel-to-oxidizer equivalence ratio of $\varphi = 0.1$ and was "air"-dilute with molar oxygen (O_2)-to-inert gas ratio of 1:3.76. The inert gases were mixtures of nitrogen (N_2) and argon (Ar) to achieve the desired test conditions. Table A1 of the appendix summarizes the mixture compositions, state conditions and ignition delay time results of the study. The base mixture was chosen due to the demonstrated strong, homogeneous ignition behavior (where strong ignition was defined as per Mansfield and Wooldridge [11]). Strong homogeneous ignition behavior is vital to chemical kinetics studies. Additionally, the base mixture of H_2 and CO exhibited two distinct stages of ignition in the temperature and pressure region of interest. The trace amounts of siloxanes used in the study are higher than what has been found in landfill gas and other biogas sources. However, the higher siloxane concentrations allow more observables to be detected and thereby provide greater understanding of siloxane chemical kinetics. Additionally, the 100 ppm levels of HMDSO and TMSO used in the current work are still sufficiently small that the siloxane chemistry is dominated by the interaction with syngas and air and not self-reaction. So, in that respect, the chemistry is expected to be directly relevant to lower siloxane concentrations found in biogas.

The mixtures were made in a dedicated stainless-steel mixing tank and the compositions were determined by using the partial pressures of the constituents as measured using a capacitance manometer gage (MKS Baratron Model 690A13TRB). The amounts of HMDSO and TMSO were calculated to yield mole fractions of 100 ppm of the organic silicon species relative to the total gas mixture. The gases used for the mixtures were ultra-high purity (99.993%) O_2, ultra-high purity Ar, ultra-high purity N_2, prepurified grade H_2 and ultra-high purity (99.9%) CO, all obtained from Purity Plus. The TMSO and HMDSO were from Sigma Aldrich with purities of ≥97.5% for the TMSO (CAS Number 1066–40–6) and ≥98.5% for the HMDSO (CAS Number 107–46–0). Each mixture was stirred continuously for at least one hour prior to the ignition experiments.

Ignition experiments were performed using the RCF to produce pressures of approximately 9–10 atm with a temperature range of 1010 K to 1060 K. A thorough description of the device and studies characterizing the RCF performance are detailed in He et al. [12] and Donovan et al. [13]. A brief description is provided here. The RCF consists of three sections: the driver section and the driven section, which are separated by a fast actuating globe valve, and a test section which is connected to the open end of the driven section. A free piston is installed at the upstream end of the driven section and in front of the globe valve, to drive the rapid compression of test gas mixture. Prior to compression, the test volume is evacuated with a pump and filled with the desired test gas mixture. The driver section is then pressurized and the globe valve is opened. The pressure launches the free piston down the length of the driven section, rapidly compressing the test gas into the test section volume which is ~50 mm long with a 50 mm diameter cross-section. The cross-section of the driven section decreases before the test section (via a convergent section) so the nose cone of the free piston achieves an annular interference fit to seal the test section. At the end of compression, the test section is filled with a uniform mixture which has been isentropically compressed to the desired state conditions, i.e. the targeted end-of-compression pressure and temperature. The test section is instrumented with a piezoelectric pressure transducer (6125B Kistler, Amherst, NY) and charge amplifier (5010 Kistler, Amherst, NY) to collect pressure data. The transducer is rated to an uncertainty of ≤1% and data are collected at 100 kHz sampling frequency. The test section also has a polycarbonate endwall to provide optical access for high-speed imaging which is used to confirm homogeneous ignition behavior. A digital camera (V711-8G-MAG-C Phantom by Vision Research) with a Navitar 50 mm lens (F0.95), a Hoya 62 mm lens (2x zoom), and a Hoya 62 mm UV(0) filter is used to record the high-speed image sequences at 25,000 frames per second with the CMOS array with a resolution of 512 × 512 pixels and an exposure time of 39.3 µs.

2.2. Computational approach

The experimental study was complemented with computational simulations of the auto-ignition behavior of H_2 and CO mixtures in a constant volume chamber in order to investigate the reaction chemistry being affected by the siloxane compounds. The simulations were conducted using the constant volume adiabatic zero-dimensional homogeneous reactor model in the ANSYS CHEMKIN software suite [14] with the Li et al. 2007 [15] chemical kinetic mechanism. The Li et al. mechanism has been validated extensively previously. In particular, Mansfield and Wooldridge [11] used the Li et al. mechanism to compare with UM RCF ignition data for H_2 and CO mixtures and found excellent agreement between model predictions and

Table 1
Mixtures considered in computational study.

Case	Base fuel	φ	Dilution	Added Species
1	H_2:CO = 1:2.34	0.1	Air level with N_2	–
2	H_2:CO = 1:2.34	0.1	Air level with N_2	600 ppm H
3	H_2:CO = 1:2.34	0.1	Air level with N_2	600 ppm CH_3
4	H_2:CO = 1:2.34	0.1	Air level with N_2	300 ppm CH_3 & 100 ppm OH

measured ignition delay times. Using the same computational approach as described in Mansfield and Wooldridge [11] auto-ignition delay time predictions were calculated at 10 atm for three representative temperatures (1020 K, 1035 K, 1050 K) and four mixtures. The four simulation mixtures were chosen based on the test gas mixture compositions used in the experimental study and the silicon species structures. Since a comprehensive reaction mechanism is not currently available for siloxane and silanol species, the mixtures were made to determine what the impact would be from an instantaneous decomposition of the parent molecule to some of its basic fragments. Based on previous studies by Chernyshev et al. [16] and Almond et al. [17], larger linear siloxanes decompose to smaller silicon species, thus requiring the loss of some of the organic groups from the parent molecule. Additionally, the low pressure pyrolysis study of linear siloxanes by Almond et al. [17] showed the production of various hydrocarbons including CH_3 for siloxanes with similar structures to the HMDSO used in this study. Therefore, the computational mixtures were a baseline mixture and three additional mixtures with different radical species included in addition to the baseline species. A list of the compositions is provided in Table 1.

Simulation Case 1 represents the baseline syngas experiments, while Cases 2-4 represent the instantaneous addition of the organic constituents of the siloxane species. In other words, Cases 2 and 3 are surrogates for rapid decomposition of hexamethyldisiloxane to form radicals with Case 2 representing an instantaneous source of one hydrogen from each methyl group on the siloxane and Case 3 representing an instantaneous source of the six methyl groups on the siloxane. Similarly, Case 4 represents the rapid decomposition of trimethylsilanol as an instantaneous source of three methyl groups and the one hydroxyl group for each TMSO molecule.

3. Results

3.1. Physical experiments

Typical pressure measurements from the ignition experiments of the different fuel mixtures are presented in Fig. 2. The compression stroke continuously and smoothly increases the pressure in the test section from the start of the experiment until the nosecone seats, ending compression. There is then a slight decrease in pressure after the end of compression (EOC) due to heat transfer from the test gas volume to the test section walls which is then followed by a rapid increase in pressure during the ignition event. The EOC was set as time $t = 0$ for each experiment. The pressure data was processed through an 80-point span moving average smoothing algorithm before assigning the ignition delay time. The ignition delay time was determined from each experiment using the pressure time-history data and the corresponding dP/dt data which were calculated using a central differencing algorithm. As shown in Fig. 2, the ignition delay time was defined as the time from the EOC to the time of the maximum of the pressure time derivative. For experiments where two stage ignition was observed, the time of the first stage of ignition was defined as the time from EOC to the time of the first local dP/dt maximum, and the time of the second stage of ignition was determined as the time from EOC to the time of the second local dP/dt maximum. When reporting the overall ignition delay, the second maximum was used for conditions where two stage ignition was observed. Uncertainty in the ignition delay time measurements primarily results from the smoothing algorithm and the bounds were defined independently for each experiment by varying the smoothing algorithm span by ±25%. Additional uncertainty was defined for each experiment by considering the range for reasonable assignment of

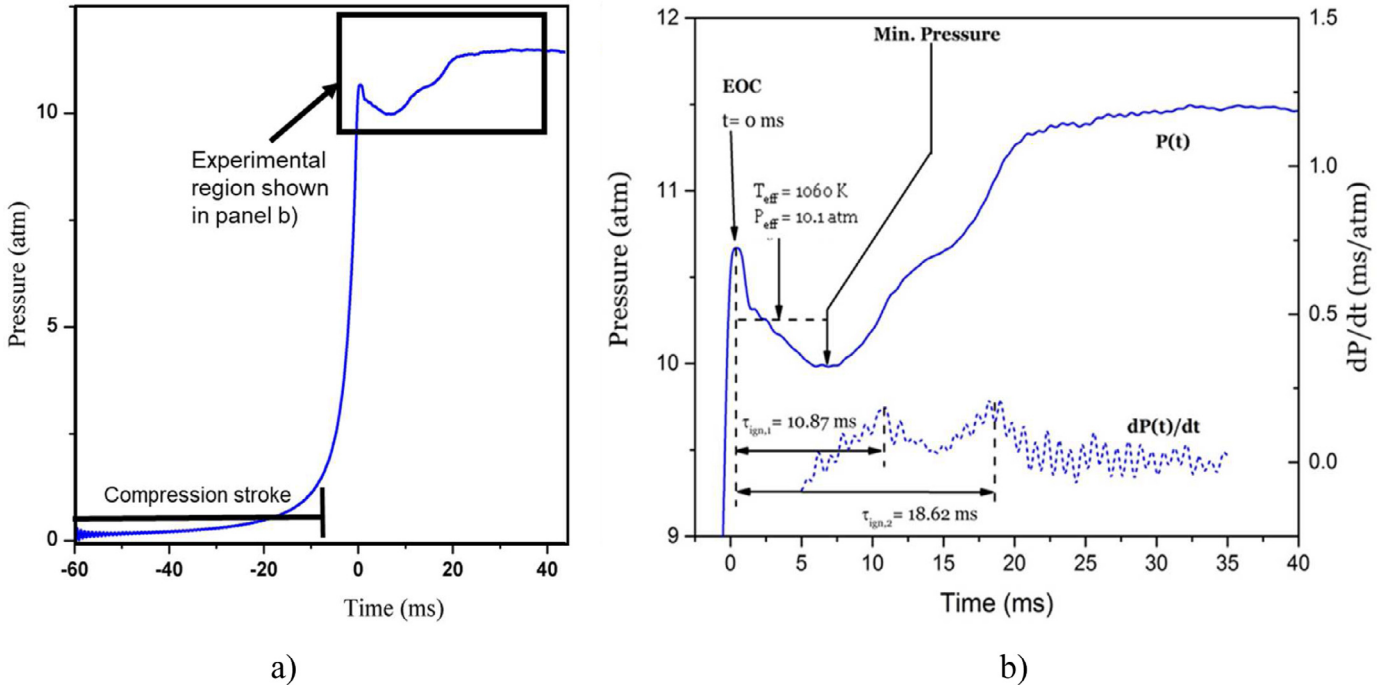

Figure 2. Typical results for pressure time history and pressure derivative for the experimental conditions of P = 10.1 atm, T = 1060 K, for a base mixture of H_2 and CO with no siloxane. $\tau_{ign,1}$ and $\tau_{ign,2}$ are the first and second stage ignition delay times respectively.

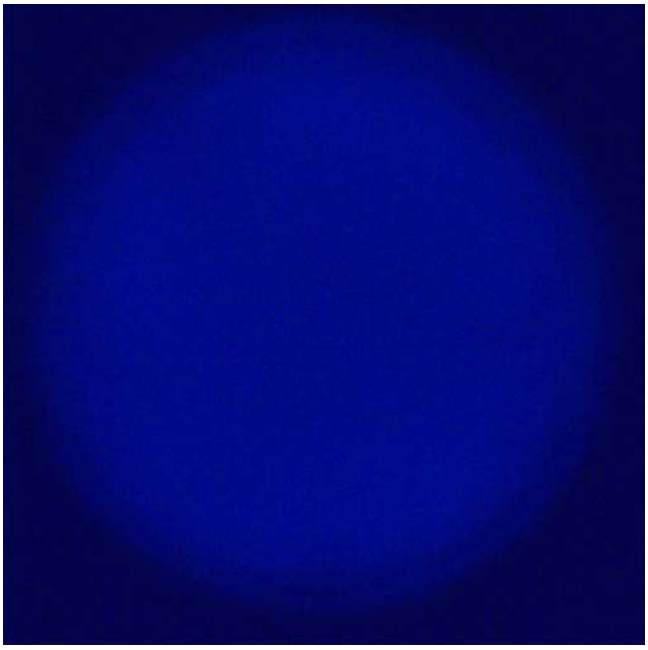

Figure 3. The image shows homogeneous chemiluminescence within the reactive core of the test section resulting from ignition of a mixture of H_2 and CO at P=10.1 atm, T=1060 K, φ=0.1.

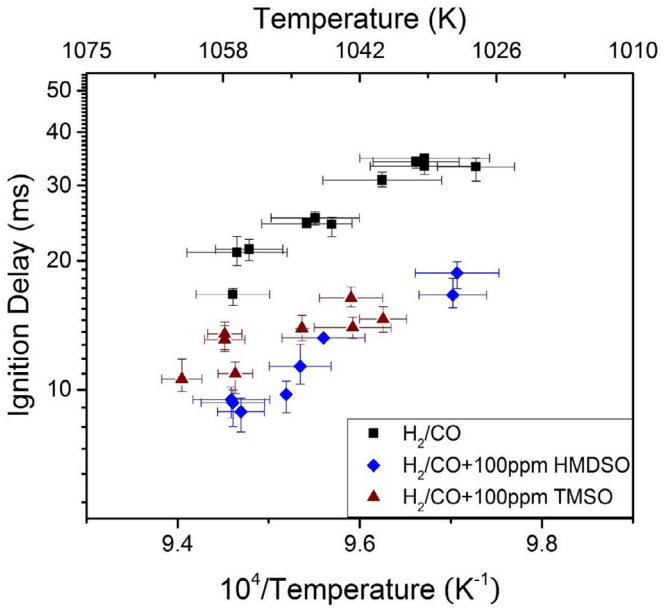

Figure 4. Experimental results for ignition delay times for P = 8.7-10.25 atm. The error bars represent the uncertainties in the ignition delay time measurements and the assigned temperatures. See text for details.

the dP/dt maxima. The resulting uncertainty for τ_{ign} was approximately ±5%.

For each experiment, a thermodynamic state was assigned using the following process. The pressure was measured directly and the temperature within the test section was calculated using isentropic compression relations and the properties of the test gas mixture. Donovan et al. [13] experimentally verified an isentropic compression process well represents the initial compression stroke of the core region of the gases in the test section of the RCF. The uncertainty in the calculated temperature is ≤ 0.4% and is due to the uncertainty in the pressure measurement. In order to account for the small decrease in pressure and temperature between the EOC and the minimum pressure before ignition, P_{min}, an effective temperature and pressure state were assigned by taking the arithmetic mean of the pressure measured from EOC to P_{min} and then calculating the temperature assuming an isentropic expansion from the EOC state to the effective pressure. Assigning effective temperature and pressure in this manner has been applied in previous experiments using the UM-RCF for similar fuels [11,18] and other ignition studies [12,19]. The assignment of an effective thermodynamic state allows for incorporation of the heat transfer effects while maintaining clarity in reporting and was discussed in detail by Mansfield and Wooldridge [11].

High-speed imaging was used to confirm the homogeneity of the ignition at the test conditions studied. Figure 3 shows a typical image of the chemiluminescence resulting from ignition of a fuel mixture of H_2 and CO, specifically corresponding to the experimental results presented in Fig. 2. The uniformity seen throughout the image illustrates that the data collected represent the behavior of the entire reactive core and not a local region or non-spatially uniform event. In other words, homogeneous or strong auto-ignition dominated the conditions studied.

The experiments in the study had pressures in the range of 8.7-10.25 atm with corresponding temperatures in the range of 1010-1060 K. A summary of the results for the auto-ignition delay times is presented in the Arrhenius diagram in Fig. 4. A list of the results is also presented in the appendix in Table A1. The results show a dramatic increase in reactivity and thus decrease in ignition delay time due to the addition of HMDSO and TMSO in comparison with the baseline mixture of H_2 and CO.

The addition of both HMDSO and TMSO promoted ignition by reducing the ignition delay time. The addition of HMDSO reduced the baseline H_2 and CO mixture ignition delay time by approximately 50%, while TMSO reduced the H_2 and CO mixture ignition delay time by approximately 37% when compared at similar state conditions. In addition to reducing ignition delay time, the 100 ppm of siloxanes also increased the pressure rise and pressure rise rate considerably, as seen in Fig. 5, which presents pressure time histories and pressure time derivatives for three experiments at comparable state conditions and using the different fuel mixtures.

3.2. Computational results

No elementary reaction mechanism currently exists for the combustion of siloxanes. In order to understand the potential effect of siloxanes on H_2 and CO ignition the following process was used. Reactant mixtures for use in simulations were determined based upon the structure and concentration of the trace silicon compounds in the experimental mixtures and a syngas reaction mechanism [13] containing 21 species and 93 gas phase reactions was used to represent the H_2 and CO ignition chemistry. Predicted ignition delay times using initial mixtures of H_2, CO and the potential radicals from the siloxane compounds, omitting any Si species, were evaluated at conditions representative of the experimental study. The weakest bond in the HMDSO structure is the carbon-silicon bond, followed by the carbon-hydrogen bond, and the strongest bond is the silicon-oxygen bond [20]. Looking solely at thermal decomposition based upon bond energies, the most likely decomposition step for the HMDSO or the TMSO would be methyl loss. Based on this assumption, 600 ppm of CH_3 was used to represent instantaneous decomposition of the HMDSO to release all methyl groups. Similarly, 300 ppm of CH_3 and 100 ppm of OH was to represent instantaneous decomposition of the TMSO to release the methyl and hydroxyl groups. The release of H atoms represents an unlikely scenario of siloxane decomposition, but it was also considered in the computational study. Since this path was considered improbable, only 600 ppm of H was evaluated and

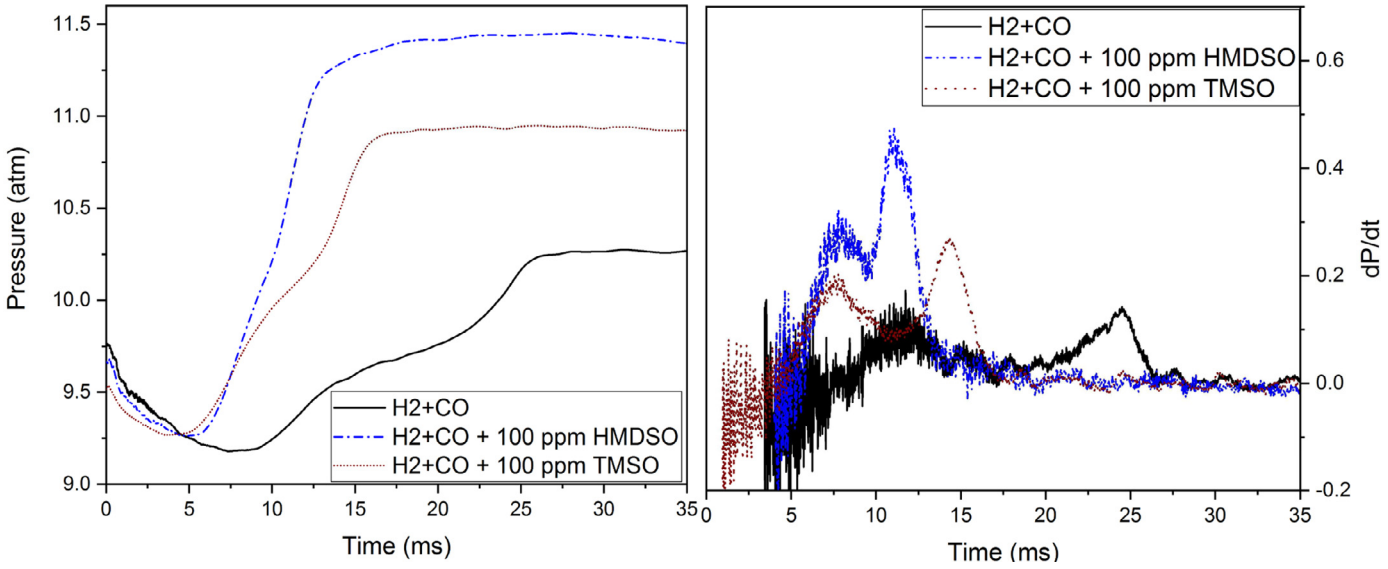

Figure 5. Pressure time histories and corresponding dP/dt data for experiments with comparable state conditions: H_2+CO with P = 9.4 atm and T=1045 K, H_2+CO+100 ppm HMDSO with P = 9.4 atm and T = 1050 K, and H_2+CO+100 ppm TMSO with P = 9.4 atm and T = 1040 K.

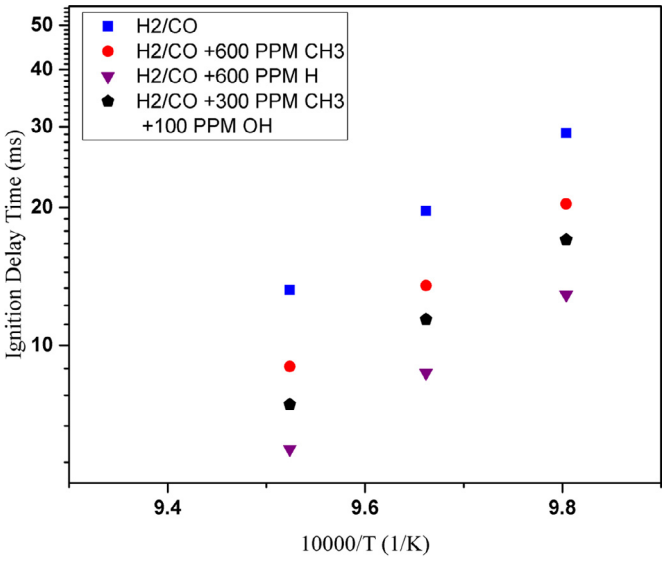

Figure 6. Effects of different initial mixture compositions on predicted ignition delay times for CO and H_2.

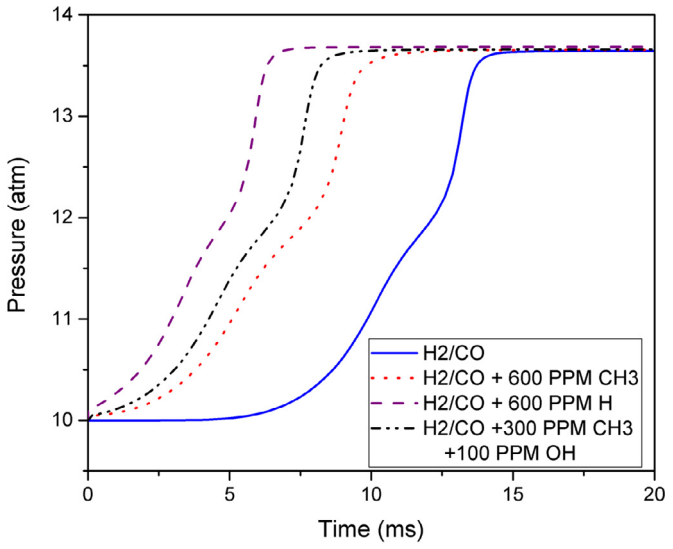

Figure 7. Effects of different initial mixture compositions on simulations of CO and H_2 ignition for an initial temperature of 1050 K.

not the total amount of H atoms available in either siloxane compound.

In order to understand if the changes in auto-ignition behavior could be attributed to the addition of these radicals, the pressure time history and ignition delay time for four representative mixtures were studied using the CHEMKIN zero-dimensional homogeneous reactor model with constant volume and adiabatic constraints [14]. The overall ignition delay times in the simulations were defined as the time from the start of the simulation to the time of the second pressure inflection point or the second dP/dt maximum. Figure 6 shows the predicted ignition delay times for each condition, and Fig. 7 shows the pressure time histories for the different mixtures at 1050 K and 10 atm.

4. Discussion

4.1. Physical experiments

For the mixture compositions and pressure and temperature range explored in this study, all auto-ignition experiments demonstrated two stage ignition behavior where two distinct dP/dt local maxima could be identified. Mansfield and Wooldridge [11] were the first to experimentally observe the distinct two stage ignition behavior of H_2 and CO mixtures. Mansfield and Wooldridge used computational simulations to interrogate the H_2 and CO ignition behavior and attributed the two stages to differences in the characteristic reaction times (and the associated reaction chemistry) of H_2 and CO at the state and mixture conditions studied. Essentially, the hydrogen gas reacts more readily than the carbon monoxide creating two distinct stages of heat release and pressure rise. Furthermore, model simulations indicated the first stage of ignition was associated with formation of H_2O_2 and HO_2, while the second stage of ignition was associated with OH and O radicals. By using conditions that exhibit separate stages of ignition in the current work, the effects of TMSO and HMDSO on specific reaction pathways may be clearer.

Looking more closely at the pressure data in Fig. 5, there is a noticeable difference between the behavior observed in the experiments with HMDSO, those with TMSO, and the baseline syn-

gas fuel case. The dP/dt data show both the first and second stages of ignition are accelerated for the HMDSO and TMSO cases relative to the base fuel case. The dP/dt for the mixtures with trace concentrations of HMDSO is higher than that of both the baseline case and the case with trace concentrations of TMSO - indicating a faster ignition event. Additionally, the overall dP/dt due to ignition is greater in the cases with organic silicon compounds than in the base fuel case. The overall dP/dt is highest for the mixtures with trace concentrations of HMDSO, followed by the mixtures with trace concentrations of TMSO and then the lowest overall rate of pressure rise is associated with the baseline case. As negative temperature coefficient behavior is not expected for these mixtures, the increased energy release in the first stage which leads to higher temperature should accelerate the kinetics of the second stage, which is consistent with the experimental data in Figs. 4 and 5, and the effects are significant. Due to the relatively low concentrations of siloxane added to the reactant mixtures, it is highly unlikely that the effects are entirely attributable only to the additional energy content from the trace species and there are more complex interactions at play in the reaction pathways. For example, since the main way for the compound to contribute energy to the system is through breaking bonds, bond energy calculations were used to make coarse estimates of the energy content of the siloxanes. Since exact energies for these compounds are not available, these calculations were based upon using average bond dissociation energies for each specific bond in the molecule (for example, the average energy for an Si-O bond across multiple molecular configurations). This will not be as accurate as characteristic bond dissociation energies for each compound since it does not specifically account for the structures and interactions but provides a coarse estimate of the energy contribution. The results indicate a less than 3% increase in the total fuel energy with the addition of 0.25% of HMDSO and less than 2% increase with the addition of 0.25% of TMSO. Although the siloxanes may have relatively high energy densities, the low concentrations and air-dilute conditions result in minimal changes in the reactant mixture properties and energy. It is also valuable to note the P_{min} for the different mixtures was almost identical, indicating the HMDSO and TMSO did not affect the heat transfer and did not change the endo- or exothermicity before ignition compared with the H_2 and CO experiments.

The impact on ignition delay time provides insights into the overall reaction rates of the different mixtures. The addition of 100 ppm of HMDSO had a more significant impact on reducing the ignition delay time, with over 10% more decrease in ignition delay time compared with the decrease caused by the addition of 100 ppm of TMSO. The complementary molecular structures of HMDSO and TMSO provide points for comparison and differentiation. Both compounds contain organic functional groups with each HMDSO molecule containing six methyl groups and each TMSO molecule containing three methyl groups. The additional methyl content of HMDSO could account for the increased reactivity, but the impact of HMDSO on the ignition delay time of the base fuel is not double that of TMSO. This indicates the difference in the effects on ignition delay time is not proportional to methyl group concentration. TMSO contains a hydroxyl group in addition to the three methyl groups which could increase the reactivity beyond the methyl groups. The potential impact of the functional group concentrations on the elementary H_2 and CO ignition chemistry is explored through the computational experiments discussed in the next section.

Another significant impact on the pressure time histories is the increased energy release illustrated by the increase in the final pressure after ignition. As seen in Fig. 5, both HMDSO and TMSO increase the final pressure after ignition compared with the base H_2 and CO mixture. The addition of HMDSO shows a significant increase, with almost double the overall change in pressure (measuring from the minimum pressure after ignition to the maximum pressure of the base fuel mixture) and almost 1.5 times the pressure change resulting from the addition of TMSO. A larger energy contribution from the larger HMDSO molecule partially explains this behavior, but thermochemical data for the siloxanes is required to determine if the overall pressure increase is due to chemical equilibrium of the products or an additional outcome of changes in reaction pathways.

4.2. Computational experiments

Figure 7 presents the results of the pressure time histories of the computational simulations at an initial temperature of T = 1050 K and pressure of P = 10 atm. Recall the different mixtures represent different amounts and types of radicals included in the initial syngas mixture. As expected, including radicals in the initial mixtures decreases the ignition delay time for each case which supports the hypothesis that rapid decomposition of the silicon compounds to form radicals can be the source of the accelerated ignition. However, siloxanes as a rapid source of radicals is not sufficient to explain all the observed trends. The greatest impact was from the addition of 600 ppm H (which reduced the ignition delay time by approximately 50%), followed by the 300 ppm of CH_3 and 100 ppm of OH (which reduced ignition delay time by approximately 45%), and the 600 ppm CH_3 addition had the smallest impact (with a decrease of 30%). However, the physical experiments, showed TMSO to have a comparable or slightly lower impact on ignition delay time compared with HMDSO. The computational study representing the most probable HMDSO decomposition fragments (Case 2, with 600 ppm CH_3) yielded a longer ignition delay when compared with the results of the study representing the TMSO fragments (Case 4, with 300 ppm CH_3 & 100 ppm OH). Additionally, none of the simulations showed a significant increase in final post-ignition pressure relative to the syngas baseline case as was observed with the HMDSO physical experiments.

While the simulations are a good starting point to understand how the structure of the silicon compounds may play a role on ignition behavior, they do not represent the correct decomposition rates of the silicon species. Due to the structure of the compounds, methyl loss would appear to be favored as the silicon-carbon bond is weaker than both the silicon-oxygen bond and the carbon-hydrogen bond. However, the presence of H is predicted due to the production of H_2 and C_2H_4 in pyrolysis experiments [17], and the simulation results shown here indicate the addition of methyl groups alone does not have a significant enough impact to cause the behavior observed in the experiments. While the addition of H atoms is closer to simulating the ignition promoting behavior seen with the addition of 100 ppm HMDSO, the instantaneous release of H atoms at the start of ignition is highly unrealistic especially at the relatively low temperatures studied in these experiments. The energy required to break the bonds necessary to produce any of the radicals studied in these simulations are above the thermal energy in the system at these conditions. So, while the simulations indicate the siloxanes are most likely a rapid source of radicals causing the significant increase in reactivity of the mixtures, instantaneous thermal decomposition to H, CH_3 or OH radicals is not the defining chemical characteristic of the siloxanes.

Additional insight into the reaction pathways that may be impacted by the addition of the organo-silicon compounds can be gained by through sensitivity and rate-of-production (ROP) analysis of the base fuel mixture. Results for sensitivity and ROP analyses for H_2 and CO are presented in Figs. 8 and 9, respectively, for T = 1035 K and P = 10 atm. The ROP results in-

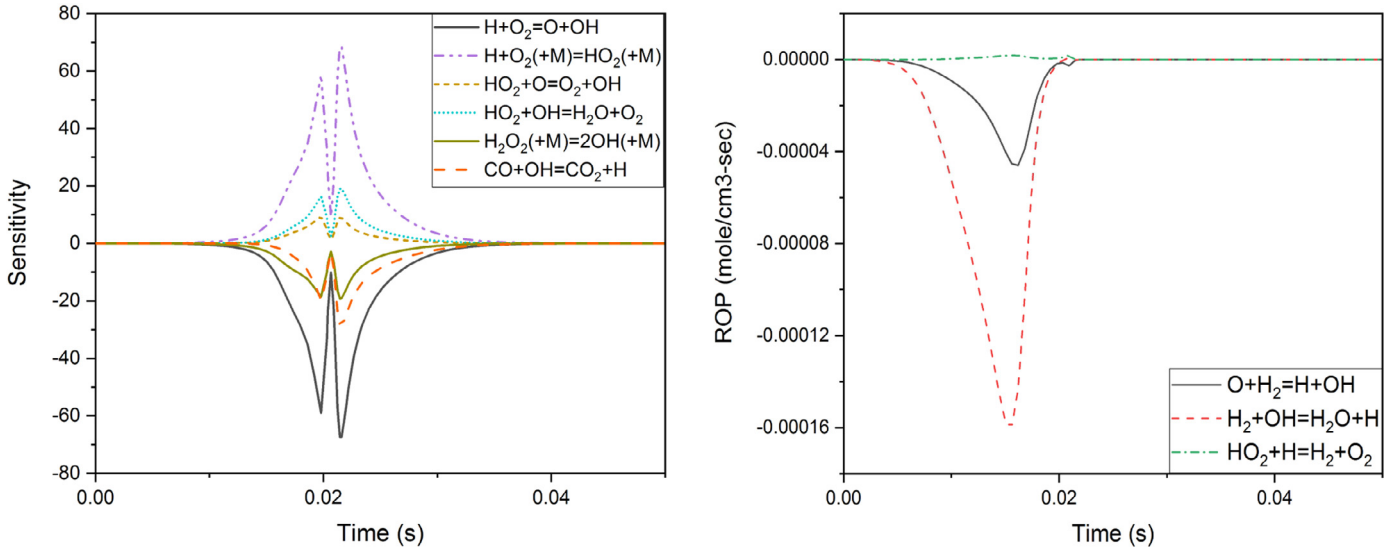

Figure 8. Sensitivity and rate of production results for H_2 for the baseline mixture of H_2 and CO at 1035 K and 10 atm.

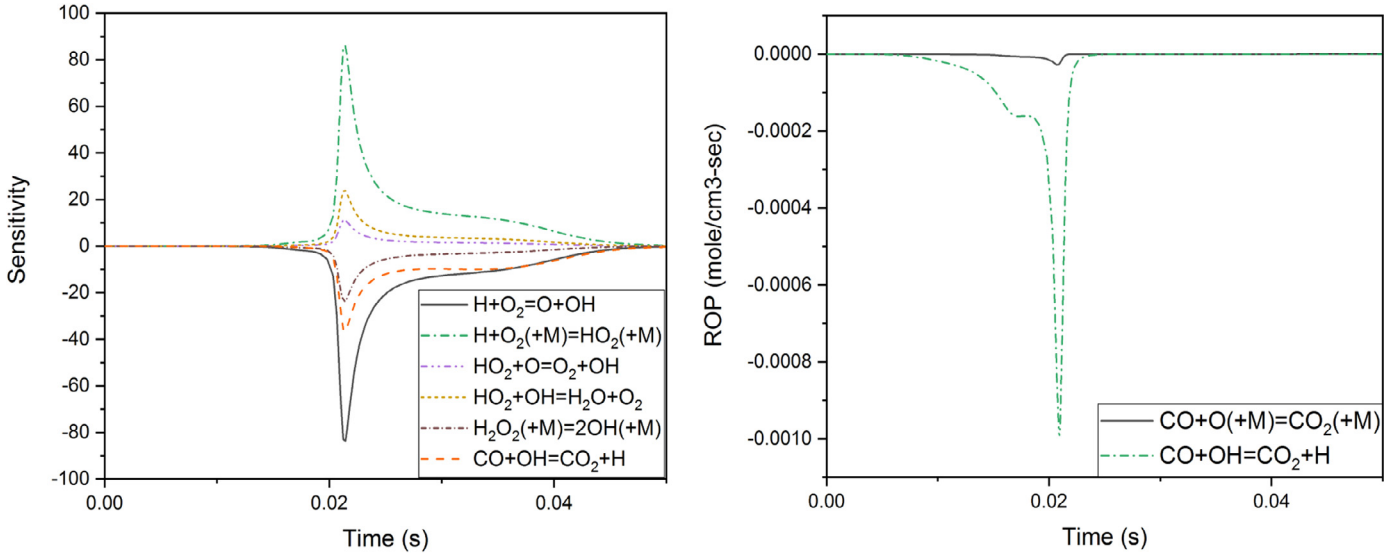

Figure 9. Sensitivity and rate of production results for CO for the baseline mixture of H_2 and CO at 1035 K and 10 atm.

dicate H_2 is primarily consumed through the $H_2 + OH = H_2O + H$ reaction followed by the $O + H_2 = H + OH$ reaction. H_2 is most sensitive to the $H + O_2 (+M) = HO_2 (+M)$ and $H + O_2 = O + OH$ reactions. Fig. 9 shows almost all of the carbon monoxide is consumed through the $CO + OH = CO_2 + H$ reaction and CO is most sensitive to the same two $H + O_2$ reactions as identified for H_2. Comparison of Figs. 8 and 9 show the H_2 is consumed in the first stage of ignition and CO is consumed in the second stage. The results also indicate OH and HO_2 are critical to forming the radical pool which leads to ignition.

Mansfield and Wooldridge [8] proposed the effects of TMSO on syngas ignition were due to reactions impacting HO_2 formation or consumption. It was hypothesized that the addition of silicon-based species enhances the consumption of and/or disrupts the formation of HO_2 resulting in increased OH production. HO_2 must be impacted by the siloxane chemistry as the pressure dependence of the syngas ignition was affected by the addition of TMSO in Mansfield and Wooldridge [8] and HO_2 chemistry was attributed as the cause of the pressure dependence. Alternatively, the siloxanes could enhance OH production which could impact HO_2 through the reactions identified in the sensitivity analysis. The physical experiments in this work and Mansfield and Wooldridge show both stages of ignition are affected by the addition of the siloxanes, and since OH is the primary radical consuming CO, that may be an indication enhance OH production is the connection with the siloxane reactions.

Based upon the experimental observations combined with the simulation results, it is proposed that reactivity is most likely initiated by radicals resulting from the combustion of the base syngas fuel. The radicals then react with the trace siloxane compounds through chain branching and propagating reactions which increase the radical pool and reactivity of the overall mixture.

Further understanding of the reaction kinetics of the organic silicon compounds is needed before definitive conclusions can be drawn on which reaction pathways are impacted by the addition of the silicon organic species. However, thermophysical data and elementary reaction chemistry for siloxane species are required to develop more accurate understanding of these systems. Once the need for siloxane thermochemistry is addressed, more specific insights into the dominant reaction pathways can be realized.

5. Conclusions

The data presented here provide new quantitative results on siloxane combustion of two important species: trimethylsilanol (TMSO) and hexamethyldisiloxane (HMDSO). Ignition experiments showed a dramatic increase in H_2 and CO reactivity due to the addition of the siloxanes HMDSO and TMSO. Significant increase in rate of pressure rise and final pressure were observed. Sensitivity and rate of production analysis indicate the mechanism for enhanced reactivity is likely via accelerated production of radicals. Since OH and HO_2 chemistry control the behavior of the base syngas mixture, it appears likely the production of OH is increased and/or HO_2 formation is suppressed by the siloxane reactions. Simulation results support the hypothesis that the siloxanes are rapid sources of radicals, but the simulations also highlight rapid, i.e. nearly instantaneous, decomposition to the basic organic radical constituents is not the only factor for the increased reactivity and the experimental observations. Thermophysical data and reaction chemistry are necessary to further understand the impact of siloxanes on combustion and ignition behaviors and to identify the reaction pathways affected by this important class of compounds.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2019.10.022.

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