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Shock tube study of methanol, methyl formate pyrolysis: CH_3OH and CO time-history measurements

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ABSTRACT

Methanol and methyl formate pyrolysis were studied by measuring CH_3OH and CO concentration time-histories behind reflected shock waves. In the study of methanol pyrolysis, experimental conditions covered temperatures of 1266–1707 K, pressures of 1.1–2.5 atm, and initial fuel concentrations of 1% and 0.2% with argon as the bath gas. Detailed comparisons of CH_3OH and CO concentration profiles with the predictions of the detailed kinetic mechanism of Li et al. (2007) [8] were made. Such comparisons combined with sensitivity analysis identified the need to include an additional methanol decomposition channel, $CH_3OH \leftrightarrow CH_2(S) + H_2O$, into the mechanism. Pathway and sensitivity analyses for methanol decomposition were performed, leading to rate constant recommendations both for CH_3OH unimolecular decomposition and H-abstraction reactions with improved model performance. In the study of methyl formate pyrolysis, methanol concentration time-histories were measured at temperatures over the range of 1261–1524 K, pressures near 1.5 atm, and initial fuel concentrations of 1% with argon as the bath gas. Our current work, and CO time-histories from previous work, indicates that the Dooley et al. (2010) [3] model is able to accurately simulate most species concentrations in shock tube experiments at early times. However, model improvement is still needed to match the CH_3OH and CO time-histories at later times. Incorporation of the modified rate constants in the methanol sub-mechanism leads to good predictions of the full methanol time-histories at all temperatures. The kinetic implications of some aspects of the CO time-histories and suggestions for further improving the predictive capabilities of these mechanisms are discussed. The current results are the first quantitative measurements of CH_3OH time-histories in shock tube experiments, and hence are a critical step toward understanding of the chemical kinetics of oxygenates.

1. Introduction

Alcohol fuels are recognized as promising renewable energy resources and are also used as additives in gasoline to reduce the formation of poly-aromatic hydrocarbon compounds, particulates, and soot [1,2]. Combustion studies of methanol, which shares many chemical kinetic characteristics with higher alcohols, can shed light on the combustion chemistry of alcohols in general. Methyl formate (MF, CH_3OCHO) is a major intermediate during the oxidation of dimethoxymethane (DMM) and may be present as a reaction product in the combustion of dimethyl ether (DME) [3]. MF is also the simplest methyl ester, belonging to a class of compounds that constitute biodiesel [3,4], and its study assists in understanding the effects of oxygenated chemical structure. Equally important, the reactions of methanol and methyl formate comprise important and fundamental subsets of detailed hydrocarbon combustion mechanisms [5,6]. Therefore, a thorough understanding of the combustion chemistry of these basic fuels is relevant for constructing kinetic models of larger oxygenated and hydrocarbon fuels.

Experimental investigations providing species time-history data describing methanol and methyl formate combustion chemistry are particularly needed. Laser absorption diagnostics, due to their fast time response and non-intrusive, *in situ* capability, are being utilized increasingly in chemical kinetic studies [7], and can be used to directly measure species concentration time-histories in shock tube experiments. These species data are critically important to efforts aimed at testing and validating large reaction mechanisms and refining their component sub-mechanisms.

In the case of methanol, Li et al. [8] have developed a comprehensive kinetic mechanism to describe the C_1 combustion chemistry (e.g., CH_4, CO, CH_2O, and CH_3OH) that involves 93 reactions and 18 chemical species. This mechanism was validated against a wide range of experimental data including shock tube ignition delays up to 4.7 atm, flow reactor speciation at pressures up to 20 atm, and laminar flame speeds at 1 atm. Refinements in the detailed mechanisms to achieve accurate simulations of the species

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time-histories during methanol decomposition are complicated by the numerous initial decomposition channels and other secondary reactions. The early theoretical study of methanol decomposition by Xia et al. [9] identified seven possible decomposition channels, but at combustion-relevant conditions, there are likely only two dominant pathways:

$$CH_3OH(+M) \leftrightarrow CH_3 + OH(+M), \quad (1a)$$

$$\leftrightarrow CH_2(S) + H_2O(+M). \quad (1b)$$

Shock tube experiments have previously been performed to measure the overall rates and individual product channels [10–13] by using very dilute mixtures (5.6–10.8 ppm CH_3OH/Kr in [10], 6.4–27.9 ppm CH_3OH/Kr in [11], 50 ppm CH_3OH/Ar in [12], and 0.48–10 ppm CH_3OH/Ar in [13]) to minimize the effects of secondary reactions. Good agreement is seen between these measurements and the recent theoretical calculations by Jasper et al. [1] using the variable reaction coordinate transition state theory (VRC-TST) method.

Besides the decomposition reactions, sensitivity analysis shows that some secondary reactions also play important roles in methanol consumption. For instance, the hydrogen abstraction reactions by atomic hydrogen consume a significant fraction of the methanol for mixtures with relatively high concentration, through the reactions:

$$CH_3OH + H \leftrightarrow CH_2OH + H_2, \quad (2a)$$

$$\leftrightarrow CH_3O + H_2. \quad (2b)$$

The rate constants for reactions (2a) and (2b) used in most of the current mechanisms are typically taken either from the expressions recommended by Warnatz [14] or those by Tsang [15], which differ by factors of 2.6 and 5 at 1200 and 1800 K, respectively. The branching ratio of these reactions, $k_{2a}/(k_{2a} + k_{2b})$, was uncertain and assumed to have a constant value of 0.8 by Warnatz [14] and Tsang [15]. Very recently, Meana-Pañeda et al. [16] performed direct-dynamics variational transition state theory calculations of $CH_3OH + H$ reactions using the microcanonically optimized multidimensional tunneling transmission coefficient. The overall reaction rate constant and the temperature-dependent branching ratio were both reported by Meana-Pañeda et al. [16]; their values were approximately one-third the value proposed by Tsang [15] and used in GRI-Mech 3.0 [17].

In the case of methyl formate kinetics, previous theoretical studies proposed the dominant decomposition channel [18,19]:

$$CH_3OCHO(+M) \leftrightarrow CH_3OH + CO(+M), \quad (3a)$$

occurring through a three-membered ring transition state. This decomposition pathway was included in the detailed kinetic model for methyl formate by Dooley et al. [3], which had been validated against experimental data from a flow reactor, shock tube ignition delays, and laminar burning velocities. This mechanism has recently been used to simulate a low-pressure (22–30 torr) laminar flame with equivalence ratios ranging from 1.0 to 1.8 [4] and to reproduce the measured methanol concentrations in these flames very closely. The authors also discussed the effects of adjusting the pressure-dependent parameters of the Rice–Ramsperger–Kassel–Marcus (RRKM) theory computed rate constants by Metcalfe et al. [19]. However, as described by the authors, considering the uncertainties in flame simulations and experiments, it was not possible to conclusively determine the pressure dependence of the chemical kinetics of MF decomposition.

Very recently, Peukert et al. [20] experimentally and theoretically determined the rate constants for hydrogen abstraction and thermal decomposition of methyl formate. In terms of the molecular channel (3a) of MF decomposition, the theoretical calculation was performed at the level of CCSD(T)/cc-PV∞Z and the master equation calculations of rate constants (1000–2000 K) were performed by considering 1-D hindered rotor treatments, tunneling corrections and a temperature-dependent energy transfer parameter $\langle \Delta E \rangle_{down}$. The theoretical predictions for $k_{3a\infty}$ are in good agreement (±30%) with the recommendations of Metcalfe et al. [19]. However, at 1 atm, the values of k_{3a}(1 -atm) in Peukert et al. [20] are 1.5–5 times the predictions of Metcalfe et al. [19] over the 1000–2000 K temperature range. In our previous shock tube study of MF decomposition [21], multi-species (CO, CH_4, and CH_2O) concentration time-histories were measured behind the reflected shock waves of MF/Ar mixtures. The CO sensitivity analysis using the Dooley et al. [3] mechanism revealed the fact that the CO concentration is dominantly controlled by MF decomposition channel (3a), enabling the measurement of k_{3a} by fitting the simulated CO profiles to the experimental data. The experiments for k_{3a} measurements span a T-range of 1187–1607 K and P-range of 0.3–5.2 atm. A weak pressure-dependence of k_{3a} was observed in the experiments for pressures higher than 2 atm. The measured values of k_{3a} by Ren et al. [21] are in good agreement with the calculations by Peukert et al. [20] (within 50%) at pressures near 5 atm, but differed by a factor of 2 or more at pressures lower than 1 atm.

The main purpose of the current study is to improve understanding of the pyrolysis of methanol and methyl formate through additional species time-history measurements and to identify areas within the kinetic models where improvements are necessary. We will first report the new results for laser-absorption-measured CH_3OH and CO time-histories behind reflected shock waves. The recent experimental and theoretical reaction rate constants for methanol pyrolysis are modified in the detailed kinetic model (Li et al. [8]), resulting in a very good fit to our experimental data. Next, the MF decomposition is further studied by including the measurement of CH_3OH concentration time-histories, which is the major intermediate. The modified methanol mechanism with high-fidelity is then used to improve the reaction mechanism for methyl formate [3].

2. Experimental setup

Our studies were performed in a stainless-steel high-purity shock tube with a 15.24 cm inner diameter. The driven section has a length of 10 m, and is separated from the helium-filled driver section (3.7 m) by a polycarbonate diaphragm (typically 0.5 mm thick). Gas temperatures and pressures behind the reflected shock waves were calculated using standard normal-shock relations and the measured incident shock speed, with a maximum uncertainty in temperature of ±1% over the test time of 1–2 ms. Between experiments, the shock tube driven section and mixing manifold were turbo-pumped at least 30 min, down to ~6 μtorr to remove residual impurities. Research grade high-purity argon (99.999% pure, Praxair Inc.) was used without further purification. Methanol and methyl formate (>99% pure, Sigma–Aldrich) were frozen and degassed three times to remove dissolved volatiles before making the mixtures. All the test mixtures were manometrically prepared in a stainless-steel mixing tank (40 L) heated uniformly to 50 °C with an internal magnetically driven stirrer.

Laser absorption and side-wall pressure measurements (Kistler 601B1 PZT) were located 2 cm from the shock tube end wall. In this study, two laser absorption diagnostics are utilized for accurate, time-resolved measurements of CH_3OH and CO concentration time-histories. These are apparently the first high-temperature CH_3OH measurements in shock tube kinetics experiments.