Ethane oxidation and pyrolysis from 5 bar to 1000 bar: Experiments and simulation

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INTRODUCTION

Ethane is important both as fuel and as an industrial feed stock for the production of more valuable materials by pyrolysis or fuel rich oxidation, as in short contact time reactors. Consequently, it is desirable to have a reliable, comprehensive model for ethane oxidation that can be used to accurately simulate processes over a wide range of mixture stoichiometries, reactor temperatures, and pressures. Such a model would have to be developed in conjunction with a good, self-consistent set of experimental data that incorporates conditions found in real reactors such as high pressures and temperatures. Until fairly recently, the upper pressure limit of experimental data reported in the literature for ethane oxidation and pyrolysis at high temperatures was around 10 bar with most experiments conducted at 2 bar or less. Higher pressure data has recently been obtained with the high pressure shock tube (HPST) at UIC that can be operated at pressures up to 1000 bar. The HPST has previously been used to study ethane oxidation and pyrolysis at 340 bar and 613 bar [1] and later stoichiometric and fuel rich oxidation at 40 bar [2]. In both studies, the experimental data were simulated using GRI-Mech 3.0 [3] and a detailed model for ethane oxidation that is an updated version of a model from Miller and Klippenstein [4] and is referred to as Miller2001 in previous work [1,2]. Both models simulated the high pressure data reasonably well particularly considering that neither model had been developed for high pressure or pyrolysis. However, the Miller2001 model could not predict acetylene concentrations very well and GRI-Mech 3.0 had some

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difficulty predicting ethane consumption for $\Phi = 1$. Neither model was able to simulate the 40 bar $\Phi = 5$ data and several modifications, discussed in [2], were made to the Miller model to achieve good predictions for these conditions. Unfortunately, these changes did somewhat degrade the prediction of the high-pressure $\Phi = 1$ data and seriously affected the simulation of the pyrolysis data. Thus a tantalizing situation existed where three models could each predict part of the experimental data spanning pyrolysis, $\Phi = 1$ and $\Phi = 5$ up to 613 bar with reasonable accuracy but no single model could handle all these cases and frequently the predictions of acetylene concentrations were poor.

In order to develop a comprehensive model that reconciles the discrepancies observed in the prior modeling work, new experimental data has been obtained in the HPST at 5, 15, 50, and 1000 bar that extends the range of the prior ethane oxidation and pyrolysis data so that it now spans 5–1000 bar overlapping at the lower pressures with experimental data from other shock tubes including that of the most recent study, which has been conducted by Hidaka et al. [5]. For pressures of 5, 15, and 50 bar, stoichiometric, $\Phi = 1$, and fuel rich, $\Phi = 5$, reaction mixtures have been used to provide data that is relevant to short contact time reactors and similar industrial processes. At a pressure of 1000 bar, $\Phi = 1$ and pyrolysis experiments have been performed supplementing previously obtained data at 340 and 613 bar. The pyrolysis experiments have permitted examination of the mechanism of ethane pyrolysis with special emphasis on accurately predicting $[C_2H_2]$ in a well-defined environment.

The new experimental data and the development of a model capable of simulating all these data will be discussed in the remainder of this paper.

**EXPERIMENTAL**

The high pressure shock tube is used to study reactions behind reflected shock waves. It is operated as a single pulse shock tube with samples of the pre-shock and post-shock gases being withdrawn into electropolished stainless steel vessels for offline analysis by a variety of gas chromatographic techniques. The shock tube, sampling methods, and analytical techniques for ethane oxidation and pyrolysis in the HPST have been fully described in earlier publications [1,6] and the same methods were used in this work. The experimental data presented here extend the pressure range to 5 bar at the low end, which is close to the upper limit of most other chemical shock tubes, and up to 1000 bar at the high end, beyond the pressure capabilities of other chemical shock tubes. In addition, a new 50 bar $\Phi = 5$ dataset is presented which is consistent with the 5, 15, 340, 613, and 1000 bar experiments and, as will be discussed later, supersedes the earlier 40 bar $\Phi = 5$ experiments [2]. Details concerning the earlier 340 bar and 613 bar experiments may also be found in [1] and 40 bar $\Phi = 5$ and $\Phi = 1$ experiments can be found in [2].

To achieve the desired reflected shock pressures, $P_b$, a variety of diaphragms have been used in the HPST to separate the $2^{\circ}$ bore driver section from the $1^{\circ}$ bore-driven section. These diaphragms burst spontaneously by increasing the helium pressure in the driver section to generate the shock waves. For $P_b = 1000$ bar, soft brass diaphragms that are 0.050" thick with two perpendicular 0.004" deep scores centered on the diaphragm are used (referred to as soft brass 50/4 diaphragms). $P_b = 50$ bar experiments are generated with aluminum 25/5 diaphragms and 15 bar with one 0.005" thick unscored aluminum foil diaphragm. A small number of experiments using two 0.005" thick, unscored aluminum foils for diaphragms have also been performed at 40 bar to exactly duplicate the conditions of the earlier 40 bar $\Phi = 5$ experiments. The 5 bar experiments were performed with unscored 0.0015" thick aluminum diaphragms.

For each individual experiment, the actual reaction pressure is obtained from a piezoelectric pressure transducer mounted in the endwall of the driven section and aligned with the long axis of the shock tube. Additionally, the reaction time is obtained from this pressure trace by measuring the time between arrival of the reflected shock wave and the reaction pressure falling to 80% of $P_b$ due to quenching by rarefaction waves generated from the diaphragm bursting [1,6].

Post-shock temperatures, $T_b$, are calculated using the chemical thermometer technique [7] to account for nonidealities in the gas behavior and real gas effects at high pressure. For each experimental pressure range, a temperature calibration has been performed that correlates incident shock velocity at the endwall of the driven section against $T_b$. The shock velocity is calculated from the time taken for the incident shock wave to pass between five pairs of piezoelectric transducers situated close to the end of the driven section and extrapolated to obtain the velocity at the endwall of the driven section.

Reagent mixtures were prepared by standard manometric methods in 50 L high-pressure mixing vessels and allowed to stand overnight before use. Mixture compositions were confirmed by analysis of samples of the reagent mixture withdrawn from the shock tube prior to each experiment. The mixtures contained 100–300 ppm ethane (Matheson gases 99.99%), oxygen (AGA, 99.995%), 150 ppm xenon (AGA 99.995%) with the balance argon (BOC, 99.999%).
oxygen was added to achieve the desired stoichiometry of \( \Phi = 1 \) or \( \Phi = 5 \), and no \( \text{O}_2 \) was added to pyrolytic mixtures. All species were used as supplied with the exception of argon which was passed over an Oxisorb trap (Matheson gases) to remove traces of \( \text{O}_2 \).

Analyses of the reagent mixtures and post-shock samples were made with standard gas chromatographic techniques using the same methodology described in [1].

EXPERIMENTAL RESULTS

1000 Bar

The major species observed in the 1000 bar \( \Phi = 1 \) ethane oxidation experiments are shown in Fig. 1a. Additionally at the highest temperatures <3 ppm of C3 and <3 ppm of C4 species were also observed. At temperatures above 1200 K CO is the main product, and \( \text{C}_2\text{H}_4 \) is the dominant product below 1200 K. Ethylene reaches a maximum between 1175–1225 K. Small steadily increasing concentrations of \( \text{C}_2\text{H}_3 \) are observed over the whole temperature range. \( \text{CO}_2 \) was not observed due to limitations of the analytical technique employed for these experiments and the carbon balance, Fig. 1c, shows a small but increasing deficit with temperature. This deficit has been observed in earlier 613 bar and 340 bar ethane oxidation experiments [1] and was shown to be due to \( \text{CO}_2 \) and not heavy species condensing in the shock tube or sample vessels. Carbon balances for both reaction mixtures are given in Fig. 1c.

For the pyrolysis experiments, the carbon balance, Fig. 1c, is very good indicating that all significant species are being recovered in these experiments. The concentration profiles for the major species in the pyrolysis experiments are shown in Fig. 1b, and similar amounts and types of minor species to those observed in the \( \Phi = 1 \) experiments were also found. Up to the highest temperatures, \( \text{C}_2\text{H}_4 \) is the dominant product passing through a maximum at 1325 K while \( \text{C}_2\text{H}_2 \) and smaller amounts of \( \text{CH}_4 \) are steadily formed until at 1425 K acetylene accounts for 45% of the products. Interestingly the scatter is very low in these experiments indicating that the high pressure shock tube is operating very cleanly at these elevated pressures for which it was specifically designed.

40 and 50 Bar

The major species profiles from the 50 bar \( \Phi = 5 \) and the 40 bar \( \Phi = 5 \) experiments from the current work are shown in Fig. 2a. At the highest reaction temperatures
In both of the current experiments a much more rapid consumption of ethane is observed above 1200K, Fig. 3, than in the earlier 40 bar $\Phi = 5$ experiments [2]. However, the ethane profiles observed in these experiments are consistent in their rate of consumption with the newly available 5 bar and 15 bar data and the high pressure pyrolysis experiments presented here and in earlier work [1]. Similarly the stable product profiles observed here ($C_2H_4$, $C_2H_2$, CO, and CO$_2$) are consistent in their shapes and maxima with the other experimental sets. The self-consistent nature of all the recent 40/50 bar data with both lower and higher pressure data suggests that the previous 40 bar $\Phi = 5$ experimental data should not be used for further model development and only the current data should be used in the future.

15 Bar

The 15 bar $\Phi = 1$ species profiles are presented in Fig. 4a. The trends are very similar to those observed in the 1000 bar experiments and are similar to the earlier 340 and 613 bar work [1]. In these experiments, the analytical technique had been modified to measure CO$_2$ in addition to the other species and small quantities of this species are also observed. The 15 atm $\Phi = 5$ species profiles, Fig. 4b show ethylene as the primary product and it reaches a maximum at around 1310 K. Acetylene and carbon monoxide are formed in almost equal proportions and steadily increase over the temperature range of the experiments until at 1375 K they observable difference in the species profiles for a given reaction mixture.

$<$3 ppm of C3 species were also observed. Carbon balances for these results are presented in Fig. 2b and are good.

Clearly these two sets of experiments are in very good agreement with each other even though very different diaphragms, both single aluminum sheet and doubled aluminum foil, and slightly different pressures were used for each set. The quoted pressures, as is normal for shock tube experiments, are nominal pressures representative of a particular dataset; the reaction pressures actually cover a small range of $P_S$. For the original and current 40 bar $\Phi = 5$ experiments, $P_S$ cover 37–41 bar and the 50 bar $\Phi = 5$ experiments 46–51 bar. Hence, although we refer to one set of experiments as 40 bar and the other as 50 bar, there is very little real difference in the $P_S$ and one would expect little if any
each account for about 20% of the species recovered. Naturally the $\Phi = 5$ species profiles lie somewhere between those observed for $\Phi = 1$ and what would be expected in pyrolysis experiments. Carbon balances for $\Phi = 1$ and $\Phi = 5$, 15 bar experiments are presented in Fig. 4c and are very good. In particular, the $\Phi = 1$ carbon balances are very good at high temperatures indicating that the inclusion of [CO$_2$] in the carbon total is sufficient to account for virtually all the carbon in the system c.f. high pressure $\Phi = 1$ experiments. Similarly to the 40/50 bar experiments small amounts of C3 species, <3 ppm total, were observed at high reaction temperatures.

5 Bar
The 5 bar $\Phi = 1$ species profiles are shown in Fig. 5a and the 5 bar $\Phi = 5$ experiments in Fig. 5b with the carbon balances in Fig. 5c. The overall trends for these experiments are very similar to the 15 bar experiments presented above. However the scatter in the carbon totals for the $\Phi = 5$ experiments is greater than normal. Nonetheless, the data is consistent with the whole range of experimental data obtained from the HPST for ethane oxidation and pyrolysis and provides overlap with the experimental ranges accessible in other shock tubes. Trace amounts of C3 species were also observed at high temperatures in these experiments.

The major species observed in the pyrolysis and oxidation experiments are the same as those observed by Hidaka et al. [5], and the species profiles are qualitatively similar although the current work spans a shorter temperature range to achieve >80% consumption of ethane. Hidaka et al. used considerably higher initial fuel concentrations, up to 5% ethane, than used in the current experiments which would lead to strong nonisothermal behavior that may account for the increased temperature range in Hidaka et al.’s experiments compared to ours. Furthermore, the reaction times in Hidaka et al.’s experiments are very different from the current work and vary from 2730 $\mu$s to 690 $\mu$s over the range 1100–1900 K for pyrolysis mixtures.

MODELING
The modeling effort in this study builds on our prior exploratory work that examined how well two unmodified, literature models GRI-Mech 3.0 [3] and a development of Miller and Klippenstein’s model [4] for formation of aromatic species from small hydrocarbons, referred to in our earlier work as Millers2001 [1,2], could simulate 340 bar and 613 bar $\Phi = 1$ and pyrolysis experiments. The earlier 340 bar and 613 bar work
Figure 5 Experimental species concentration profiles, [A], relative to \([C_2H_6]_0\), for ethane oxidation and pyrolysis at \(P_s = 5 \text{ bar}\). (a) \(\Phi = 1\); (b) \(\Phi = 5\); (c) carbon balances. For (a) and (b), closed squares, \(C_2H_6\); open squares, \(C_2H_4\); open triangles, \(C_2H_2\); cross, \(CO\); star, \(CO_2\). For (c) closed symbols preshock, open symbols postshock, squares represent \(\Phi = 5\) experiments, and triangles \(\Phi = 1\) experiments divided by 2.

clearly showed that the Miller2001 model simulates the \(\Phi = 1\) datasets well, while GRI-Mech 3.0 tended to simulate the pyrolysis data better than Miller2001. However, for pyrolysis and oxidation at both pressures, GRI-Mech 3.0 predicted the \(C_2H_2\) concentrations considerably better than Miller2001 even in situations, \(\Phi = 1\), where GRI-Mech 3.0 could not accurately simulate other species. An extension of the Miller2001 model, MillerMod1 [2], was capable of simulating 40 bar \(\Phi = 5\) data reasonably accurately. However when applied to the whole current experimental dataset, the performance of this model is poor for conditions other than the original 40 bar and \(\Phi = 5\) data presented in [2]. Thus while the modifications made to Miller2001 to generate MillerMod1 are perfectly reasonable, the lack of comprehensive application of MillerMod1 indicates that it would be an inadequate base for building a more comprehensive model and it will not be considered further. Therefore, the remainder of this discussion focuses on the application of Miller2001 and GRI-Mech 3.0 to the simulation of pyrolytic and rich oxidation experiments and on the extension of the pyrolysis model to stoichiometric oxidation conditions.

**Pyrolysis and Rich Oxidation**

The earlier studies [1] at 340 bar and 613 bar clearly showed the simulation of \(C_2H_2\) to be a problem for Miller2001 and in the current work the problem persists for the 1000 bar dataset and to a lesser extent for the 5, 15, and 50 bar \(\Phi = 5\) datasets, Figs. 6 and 9–11. A secondary problem with Miller2001 at 340, 613, and 1000 bar is that at temperatures above about 1325 K the model predicts low concentrations of \(C_2H_4\) although the temperature at which the maximum \(C_2H_2\) concentration is observed is in agreement with the experimental data. The low \(C_2H_4\) concentration could be due to either insufficient \(C_2H_2\) being formed at 1325 K and higher temperatures i.e. reaction paths leading to \(C_2H_4\) changing, or increasing consumption of \(C_2H_2\). On the positive side, the Miller2001 model generally provides pretty good predictions for ethane in the pyrolysis experiments. Figures 6–11 clearly show that GRI-Mech 3.0 provides superior predictions of the \(C_2H_2\) concentrations than Miller2001 for pyrolysis (340, 613, and 1000 bar) and rich oxidation (5, 15, and 50 bar) although the predictions for \(C_2H_2\) and \(C_2H_4\) are not so good. Initially the modeling effort focused on the differences between Miller2001 and GRI-Mech 3.0 to try and identify significant elementary reactions that would allow Miller2001 to improve the \(C_2H_4\) and particularly the \(C_2H_2\) predictions while maintaining the \(C_2H_6\) ones.

Sensitivity analyses and reaction path analyses (Fig. 12) revealed, not surprisingly, that the key to simulating \(C_2H_2\) concentrations accurately lies in the web of reactions involving \(C_2H_6\), \(C_2H_4\), and \(C_2H_2\) (Fig. 13). Naturally any alterations to these set of reactions will
Figure 6 Comparison of experimental data and modeling results from three models, 1000 bar, ethane pyrolysis. Solid squares, experimental; open squares, Miller2001; open triangles, GRI-Mech 3.0; open diamonds, modified Miller2001 without reactions 533–535.

Figure 7 Comparison of experimental data and modeling results from three models, 613 bar, ethane pyrolysis. Solid squares, experimental; open squares, Miller2001; open triangles, GRI-Mech 3.0; open diamonds, modified Miller2001 without reactions 533–535. Adapted from [1].

The reaction numbers are different thus when reaction numbers are quoted. For the 340, 613, and 1000 bar pyrolysis data it has only been necessary to adjust three reactions 132(75), 159(71), and 322(174). Frequently the reaction numbers in Miller2001 and GRI-Mech 3.0
Figure 8 Comparison of experimental data and modeling results from three models, 340 bar, ethane pyrolysis. Solid squares, experimental; open squares, Miller2001; open triangles, GRI-Mech 3.0; open diamonds, modified Miller2001 without reactions 533–535. Adapted from [1].

with GRI-Mech 3.0. Additionally the ethylene concentration shows a marked negative sensitivity to 132(75). Thus if the rate of 132(75) is reduced then it would be expected that the predicted acetylene concentration would fall and the C2H4 concentration would rise. In Miller2001 $k_{132(75)}$ is taken from the compilation of Baulch et al. [8], whereas GRI-Mech 3.0 uses the value recommended by Tsang and Hampson [9]. At 1000 K, the Baulch value for $k_{132(75)}$ is 15 times greater than that of the Tsang and Hampson value although the difference decreases to a factor of 2 at 1300 K. Knyazev et al. [10] studied the reverse of reaction 132(75) experimentally at temperatures up to 947 K and obtained values for $k_{132(75)}$ and $k_{132(75)}$ that they recommend for the temperature range 200–3000 K. The rate coefficients for 132(75) obtained from Knyazev et al. vary from a factor of 5 to 2 lower than the Tsang and Hampson values at 1000–1300 K. Simulations have been performed using the Tsang and Hampson value and the Knyazev et al. value for $k_{132(75)}$, and generally the value of Knyazev et al. leads to an overprediction of C2H2 whereas the Tsang and Hampson value with the A factor increased by 0.32E6 (25%) gives good agreement with the experimental data over the whole dataset from 5 bar to 1000 bar. At this point, extensive simulations have been made and it appears that a value of $k_{132(75)}$ somewhat higher than that recommended by Knyazev et al. is needed. Of course, a missing reaction that removes C2H4 without forming C2H3 or C2H2 could also account for the fact that a higher rate than Knyazev et al.’s is required although no such route is obvious and the carbon balances indicate all species are accounted for.

Reaction 322(174) is the direct conversion of ethylene to acetylene and hydrogen, C2H4 + M = C2H2 + H2 + M, and shows the highest positive sensitivity with respect to C2H2 concentrations in Miller2001 and the strongest negative sensitivity with respect to C2H4 concentration (Fig. 12). In Miller2001, $k_{322(174)}$ is taken from Baulch et al. [11] and GRI-Mech 3.0 again uses the Tsang and Hampson value [9] similarly to above. Over the temperature range of the present work, the Baulch et al. value for $k_{322(174)}$ is around 4 orders of magnitude greater than the Tsang and Hampson value (0.48 cm³ mol⁻¹ s⁻¹ at 1300 K) which could lead to an overprediction of C2H4 consumption and therefore to excess C2H2. The Tsang and Hampson value of $k_{322(174)}$ has been included in the model with the A factor decreased by 25%.

The final reaction of significance in the pyrolysis work is 159(71) the reaction between hydrogen atoms and acetylene to form vinyl radicals, H + C2H2 = C2H3. Similarly to reactions 322(174) and 132(75), this reaction shows a strong positive sensitivity with respect to C2H2 concentrations although it shows a weak negative sensitivity with respect to C2H4 in GRI-Mech 3.0 and does not appear in the sensitivity analysis with respect to C2H2 in Miller2001. The Miller2001 model uses rate coefficients for this reaction that are taken from Marinov et al. [12], whereas GRI-Mech 3.0 uses $k_{322(174)}$ from Payne and Steff [13] and $k_0$ from Tsang and Hampson with Troe [9] broadening.

Full text is available at: