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Combustion of CO/H₂ mixtures at elevated pressures [☆]

R. Sivaramakrishnan ^a, A. Comandini ^a, R.S. Tranter ^b, K. Brezinsky ^{a,*},
S.G. Davis ^c, H. Wang ^d

^a Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, IL 60607, USA

^b Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, USA

^c Exponent, 21, Strathmore Road, Natick, MA 01760, USA

^d Department of Aerospace and Mechanical Engineering, University of Southern California, Los Angeles, CA 90089, USA

Abstract

The high pressure oxidation of dilute CO mixtures doped with 150–200 ppm of H₂ has been studied behind reflected shock waves in the UIC high pressure single pulse shock tube. The experiments were performed over the temperature range from 1000 to 1500 K and pressures spanning 21–500 bars for stoichiometric ($\Phi = 1$) and fuel lean ($\Phi = 0.5$) oxidation. Stable species sampled from the shock tube were analyzed by standard GC, GC/MS techniques. The experimental data obtained in this work were simulated using a detailed model for H₂/CO combustion that was validated against a variety of experimental observables/targets that span a wide range of conditions. These simulations have shown that within experimental error the model is able to capture the experimental trends for the lower pressure data sets (average nominal pressures of 24 and 43 bars). However the model under predicts the CO and O₂ decay and subsequent CO₂ formation for the higher pressure data sets (average nominal pressures of 256 and 450 bars). The current elevated pressure data sets span a previously unmapped regime and have served to probe HO₂ radical reactions which appear to be among the most sensitive reactions in the model under these conditions. With updated rate parameters for a key HO₂ radical reaction $\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$, the model is able to reconcile the elevated pressure data sets thereby extending its capability to an extreme range of conditions. © 2006 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

Keywords: Chemical kinetics; Detailed model; High pressure; Shock tube; Mars in-situ propellant

1. Introduction

The Mars in-situ propellants rocket (MIPR) is a small vehicle proposed to fly autonomously on Mars, using in-situ propellant production [1]. The propulsion system will be fueled by carbon monoxide and oxygen. The overall oxidation of bone dry carbon monoxide has a high activation

energy, and therefore a slow reaction rate. However a one-dimensional kinetic computer simulation [2] shows that at the high temperatures and pressures typical of a rocket engine chamber burning CO and O₂, the reaction would be self-sustaining. The same result has been obtained in spark torch igniter tests performed at the Rocket Laboratory at NASA [2]. On the other hand, the unusually high activation energy may require more than the use of a spark to initiate and nurture the reaction until it becomes self-sustaining. One method to lower the overall activation energy is to provide a hydrogen source to the system.

[☆] Supplementary data for this article can be accessed online. See Appendix A.

* Corresponding author. Fax: +1 312 413 0447.

E-mail address: kenbrez@uic.edu (K. Brezinsky).

Detailed studies by Bond et al. [3] have been able to characterize ignition behavior for a variety of wet (>2000 ppm H_2) to very dry mixtures (<200 ppm H_2) in carbon monoxide oxidation. However their studies were performed at very low pressures (25–40 torr) and low temperatures (<1000 K). More recent experimental measurements at NASA Glenn [4] that involve the spark torch ignition of carbon monoxide and oxygen have shown that a small amount of hydrogen was necessary for ignition, but also that the amounts present in the carbon monoxide commercial source, 5 ppm (3.9×10^{-5} wt%) H_2 and 30 ppm (4.8×10^{-5} wt%) H_2O , were insufficient. Because a sonic orifice was used in order to measure and control the flow rate of hydrogen introduced in the chamber, the minimum amount of hydrogen flow rate was limited by the smallest orifice available. Therefore, it was not possible to identify the actual minimum amount of hydrogen necessary for ignition. Knowing the minimum amount of hydrogen is important for the rocket design, because it will indicate if the trace amounts of water in the Martian atmosphere would be enough for ignition or if a supplemental amount of hydrogen must be brought from Earth. A well-validated accurate chemical kinetic model could help provide the answer.

An accurate model is also an important for the determination of the key combustor design characteristics viz. combustor length, nozzle shape, and diameter. In particular, the characteristic time of the slow kinetics of combustion affects the length of the combustor needed for complete combustion. Experiments in a calorimeter chamber at NASA [5] indicate that combustion, measured by the heat flux, continued throughout the chamber for the experimental conditions studied, so that incomplete combustion occurred inside the chamber. Another important component of a rocket engine that must be designed and optimized is the engine nozzle. In particular the performance measured by the specific impulse, which is the amount of thrust for the weight of burned fuel, was found to be very sensitive to the nozzle geometry. An accurate and validated chemical kinetic model at the extreme conditions, 200–300 psi for pressure fed engines and 2000–3000 psi for turbopump fed engines, at which the rocket engine is proposed to be operated could provide the necessary information for the choice and design parameters for an optimum geometry of the rocket nozzle.

The goal of our experimental and modeling studies is thereby twofold:

- a. Detailed experiments and validated model predictions at rocket engine conditions.
- b. Estimate through experiments and subsequent modeling the minimum amount of H_2/H_2O required for ignition.

The principal focus of the present work is to address the first goal; viz. high pressure experiments and detailed modeling of the CO/H_2 system.

2. Background studies

Apart from the Bond et al. [3] studies and the studies performed at NASA [1,2,4,5] prior experimental studies on the CO/H_2 system are limited to the atmospheric pressure flame speed measurements by McLean et al. [6] and Vagelopoulos and Egolfopoulos [7], detailed shock tube ignition delay measurements at 1.5–2 atm by Dean et al. [8] and the species profile measurements from the moist CO oxidation ($CO/H_2O/O_2$) system at pressures from 1 to 10 atm in a turbulent high pressure plug flow reactor by Kim et al. [9]. There are no higher pressure studies in the literature on the CO/H_2 system, specifically at the high pressure, high temperature conditions encountered in the rocket engine, thereby necessitating the present detailed study in the high pressure shock tube.

The majority of experimental and detailed modeling studies that have been performed to date on the $CO-H_2-H_2O-O_2$ system have been summarized in a recent article on the modeling of H_2/CO combustion [10]. This modeling effort incorporates the most recent kinetic and thermochemical information and has utilized an optimization technique to account for the available experimental targets. Since this detailed model has been developed there has been a recent study by Saxena and Williams [11] who have developed and validated a detailed model against premixed and diffusion flame data (primarily flame speed measurements, flame structures, and extinction) and autoignition data. However the Davis et al. [10] model represents a more comprehensive modeling effort that reconciles more stringent validation targets such as species concentration profiles and forms a more appropriate basis for modeling the current experimental data viz. species profile measurements from the single pulse shock tube.

3. Experimental

3.1. Shock tube

The UIC high pressure shock tube (HPST) is operated as a single pulse shock tube with experiments performed behind reflected shock waves. The design and mode of operation of the shock tube has been described in detail in earlier publications [12–14] with the present experiments performed with only minor changes to the setup that involve the use of heated sample vessels, mixture rigs and a heated analytical rig. The present

sets of experiments were performed with a 101" long driven section with the diaphragm section separating it from a 60" long driver section. The driver section length is made variable by the insertion of brass plugs in order to obtain best possible cooling rates (7×10^4 – 1.5×10^5 K/s). A dump tank placed just ahead of the diaphragm section on the driven side rapidly quenches the reflected shock wave thereby permitting the shock tube to be operated in single pulse fashion. The present set up gave reaction times in the range 1.1–2.0 ms for the data sets with exact reaction times measured for each experiment. Incident shock velocities were calculated from the response of pressure transducers (PCB Piezotronics) located in the side wall of the shock tube to the incident shock wave and these velocities have been correlated with the temperature in the reaction zone using the chemical thermometer technique [13,14]. Reaction pressures and reaction times [12–14] are obtained from a pressure trace recorded from a pressure transducer mounted in the end wall of the driven section parallel to the long axis of the shock tube. Prior to each experiment, the driven and the sampling sections of the shock tube were evacuated to 1×10^{-5} torr by means of two sets of rotary-pump/turbo-pump combinations and a separate rotary pump was used to evacuate the driver section.

3.2. Reagents

Reagent mixtures consisting of carbon monoxide, 408–540 ppm (99.999%, advanced specialty gases), oxygen, 300–810 ppm (99.999%, AIR-GAS), hydrogen, 160–225 ppm (99.999%, AIR-GAS) diluted in the bath gas, argon (99.999% and 99.9995%, AIRGAS) were prepared manometrically in 50 L vessels and allowed to stand overnight before use. CO, O₂, and H₂ were used as supplied but the bath gas argon was passed through an Oxisorb filter before admission into the mixture tank. The CO system is very sensitive to the presence of impurities. However since only a few hundred ppm of the reagents (CO, O₂, and H₂) are used in this study the impurities in the reagents are only a few ppb or less and therefore would have a negligible effect in comparison to the impurities in the bulk gas Argon. To test for the effect of impurities in our experiments two grades of Argon were used: one with a rated purity 99.999% (main impurities are 1 ppm moisture, 1 ppm H₂) and the other 99.9995% (1 ppm moisture). There was no discernible effect in using the higher purity mixture in these experiments since the actual amounts of H₂ dopant were about 160 ppm or higher and 1–2 ppm total hydrogenous impurities should have no significant effects. However for future experiments involving estimating the minimum H₂/H₂O required for ignition we propose to use a high pressure purifier

assembly (see Ref. [15] for a detailed discussion of impurities and the high pressure purifier system to be used) that can reduce the impurities to ppb levels.

3.3. Analysis

Pre and post shock samples were withdrawn into electropolished stainless steel vessels via a port located in the endwall of the shock tube and analyzed offline using standard gas chromatographic (GC) and mass spectrometric (MS) techniques. The analyses were performed by simultaneously injecting the gas samples via gas sampling valves onto two columns. A PLOT-Q column (30 m \times 0.320 mm \times 20 μ m, Agilent) eluting into a FID through a nickel catalyst (used for detection and quantification of CO and CO₂) and a thick MOLSIEVE 5A column (30 m \times 0.540 mm \times 50 μ m, Agilent) eluting into a TCD (detection and quantification of permanent and rare gases) were used for the analysis. Excellent baseline separation was achieved for all the observed intermediates. Identification of reaction products was achieved by retention time matching as well as with the aid of the MS. The detectors were calibrated using calibration standards where available and the calibrations were checked periodically for consistency.

One important modification that was deemed essential for measurement of oxygen was the use of argon, rather than helium, as the carrier gas for the TCD. With helium as the carrier gas it is essentially impossible to achieve baseline separation of trace oxygen from the argon bath gas as in our current experiments without recourse to exotic column phases [16] or subambient column temperatures. Consequently the only solution was the use of argon as the carrier gas for the TCD in order to detect O₂ as an eluent above the baseline of argon. Apart from O₂ analysis, with this technique we were also able to detect any helium that is present in our samples thereby removing the need to add neon as a diluent to test for driver gas dilution as we have done previously [13].

However the use of argon as the carrier gas greatly decreases the sensitivity of the TCD and consequently detection of small amounts of H₂ (~100 ppm) in our post shock samples was not possible. We have recently installed a sensitive helium photoionization detector (in order to monitor low-sub ppm levels of H₂ in our samples) that is essential for future work with reduced amounts of H₂ to estimate the minimum H₂ required for ignition.

4. Experimental results

CO oxidation experiments were performed over a wide temperature range 1000–1500 K for

stoichiometric ($\Phi = 1$) and fuel lean ($\Phi = 0.5$) mixtures. Experiments were performed over a wide pressure range from 21 to 500 bars that encompasses the operating range of the proposed MIPR engine. Seven sets of data, four data sets at nominal pressures of 24, 43, 256, and 450 bars for stoichiometric oxidation, three data sets at nominal pressures of 24, 43, and 256 bars for fuel lean oxidation, and comprising more than 150 experiments were performed (Pressures refer to average pressures for each data set, however the exact reaction pressures for each experiment are shown in the [Supplementary material](#) and these have been used for all the simulations that have been performed in this work). The reaction times for these experiments range from 1.1 to 2.0 ms (Refer to [Supplementary material](#) for exact reaction times). Heat release due to exothermicity is minimized (<10 K temperature rise) since dilute mixtures have been used and consequently essentially isothermal conditions are obtained in the experiments.

Profiles for CO, CO₂, and O₂ were obtained for all the experiments. Good carbon totals (being within 5% at the lower temperatures and no more than 12% at the highest temperatures in this study) were obtained for the data sets in this work. The increased discrepancy in the carbon totals is due to the increased error ($\pm 10\%$) in detecting and quantifying CO₂ by means of the nickel catalyst/FID assembly in contrast to the more accurate ($\pm 5\%$) direct TCD measurements for CO. Representative species profiles at 24 and 256 atm for the $\Phi = 1$ and $\Phi = 0.5$ data sets are shown in [Figs. 1 and 2](#), respectively. CO starts to decay at around 1200 K with a corresponding CO₂ increase being observed for all the experiments. O₂ decay is observed approximately 50 K earlier than the temperatures at which CO decays

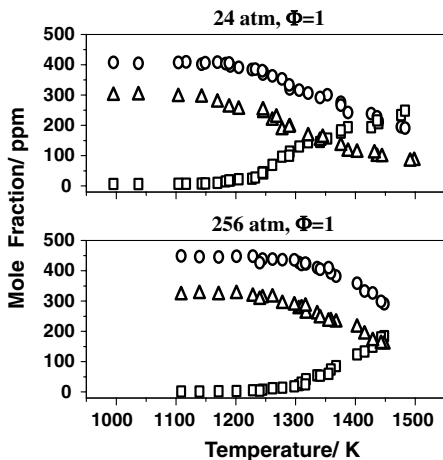


Fig. 1. CO oxidation data, $\Phi = 1$. [O], CO; [Δ], O₂; [\square], CO₂.

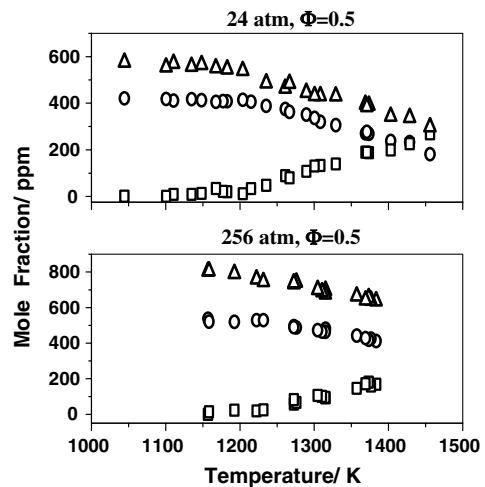


Fig. 2. CO oxidation data, $\Phi = 0.5$. [O], CO; [Δ], O₂; [\square], CO₂.

for all the data sets. Similar trends are observed for the experiments performed at nominal pressures of 43 and 450 atm (not shown in the figures). [Figure 3](#) depicts the effect of stoichiometry on CO decay for the experiments at 24 and 256 atm. No discernible difference is observed in the species profiles from the stoichiometric to the fuel lean mixtures for the 24, 43 (not shown in the figure), or 256 atm data sets. On the other hand as the pressure is raised from 24 to 256 atm a slower decay for CO and a corresponding slower rise for CO₂ is observed, for example for the 24 atm $\Phi = 1$ experiments CO begins to decay at 1200 K whereas for the 256 atm $\Phi = 1$ experiments a slower decay is observed with CO beginning to react only at temperatures close to

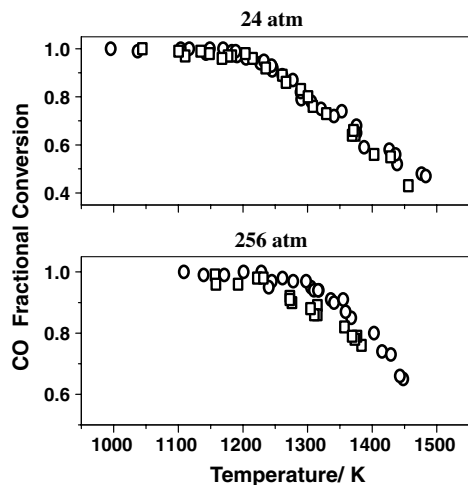


Fig. 3. CO oxidation, effect of stoichiometry. [O], $\Phi = 1$; [\square], $\Phi = 0.5$.

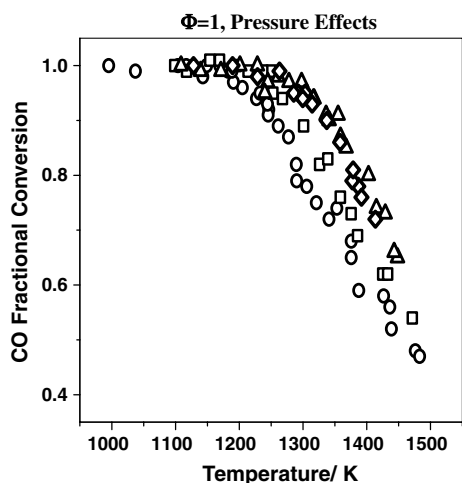


Fig. 4. CO oxidation data, $\Phi = 1$. [O], 24 atm; [□], 43 atm; [△], 256 atm; [◇], 450 atm.

1300 K. These observations reflect trends similar to that observed in the moist CO oxidation ($\text{CO-H}_2\text{O-O}_2$) experiments in the Princeton Plug Flow reactor [9] with a slower rate of CO decay observed as the pressure was raised from 1 to 10 atm. No significant difference can be observed when the pressure is further raised from 256 to 450 atm indicating that reactions have attained their high pressure limit at 256 atm. A similar trend is observed for the $\Phi = 0.5$ data sets with the CO decay and corresponding CO_2 buildup

being slower as the reaction pressures are raised. Figure 4 depicts the fractional conversion of CO plotted as a function of temperature for the $\Phi = 1$ data sets and clearly elucidates the effects of reaction pressure on CO decay.

5. Modeling

Preliminary simulations for the single pulse shock tube data were performed using the CHEMKIN 3.6 [17] suite of programs. These simulations used two reaction models: the recently optimized H_2/CO oxidation model of Davis et al. [10], hereafter referred to as the base model, and GRI-Mech 3.0 [18]. Though the GRI-Mech is a model for natural gas combustion, it also incorporates targets relevant to CO-H_2 chemistry. The base model of Davis et al. [10] was specifically optimized against reliable H_2 and CO combustion data. Preliminary simulations shown in Fig. 5 for the $\Phi = 1$ data sets indicate that the base model is able to reproduce the temperature at the onset of observable reaction. At higher temperatures, the model tends to give slower oxidation rates compared to the experimental observation.

On the other hand, for the lower-pressure experiments GRI-Mech 3.0 tends to predict temperatures for the onset of reaction that are too high compared to experimental observation. In addition, the model predictions do not exhibit the pressure effect observed experimentally (see Figs. 4 and 6). Thus the closer agreement between

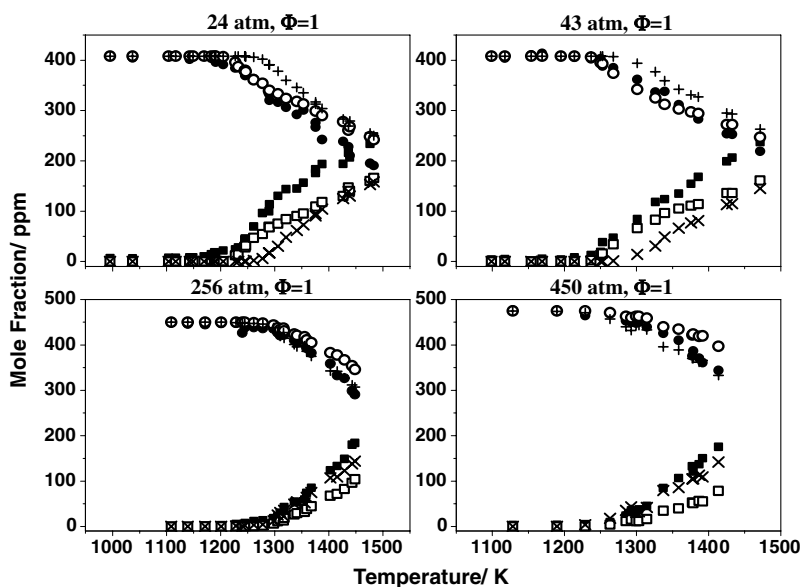


Fig. 5. [●], Expt. CO; [■], Expt. CO_2 ; [○], base model CO; [□], base model CO_2 ; [+], GRI-Mech 3.0 CO; [×], GRI-Mech 3.0 CO_2 .

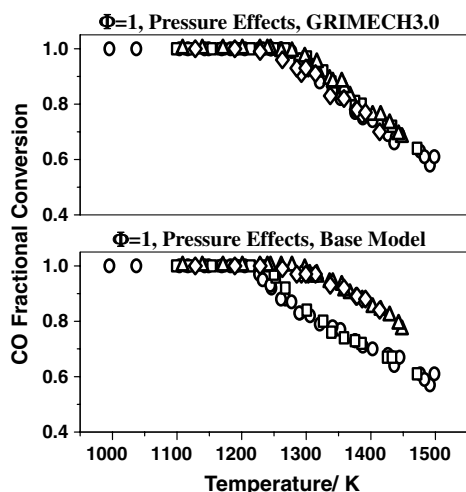
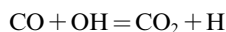
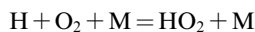
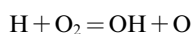


Fig. 6. Pressure effects, [O], 24 atm; [□], 43 atm; [△], 256 atm; [◇], 450 atm.

the experimental observations and model predictions at 256 and 450 atm may be fortuitous. On the other hand the base model shows the qualitative pressure effect trends (Fig. 6) exhibited in the experimental data (Fig. 4).

For these higher-pressure experiments, the base model exhibits smaller CO decay rates than experimentally observed. Similar trends are observed for the O_2 decay profiles for the $\Phi = 1$ data sets as well as for the species profiles in the $\Phi = 0.5$ experiments. The sensitivity coefficients of the CO concentration to each reaction in the base model were determined by the brute-force method at approximately 1400 K. As expected, the CO concentration was the most sensitive to



under all pressure conditions. The rate coefficients of these reactions have been extensively studied. Within their remaining uncertainties [10] there was no possibility to reconcile the prediction with the experimental data over the entire pressure range. Specifically for the reaction between CO and OH, the most dominant CO decay channel, even the addition of a high pressure channel forming the HOCO adduct followed by its subsequent decomposition to $CO_2 + H$ cannot account for the experimental data.

Because of the elevated pressures in the present study, reactions involving the HO_2 radical start to become the next most influential reactions for the CO concentration at 256 and 450 atm, even at the

upper temperature range of 1400–1500 K. These reactions from Ref. [10] include



and to a lesser extent



The base model used the rate coefficient of Kim et al. [9] for reaction 24 on the basis of moist CO oxidation experiments. The uncertainty for the rate coefficient is perhaps larger than about one order of magnitude at the temperature of interest to the current study. For example, the rate coefficient evaluation of Tsang and Hampson [19] gives an expression which is almost one order of magnitude larger than the values of [9]. Indeed the high-pressure (256 and 450 atm) data could be successfully reconciled by employing the higher rate values of [19], but the 1–10 atm turbulent flow reactor data [9] cannot be reconciled with the inclusion of this higher rate coefficient for reaction 24.

Therefore, we focused our analysis on the second reaction (15). The rate coefficient shows a very strong and peculiar temperature dependence (see Fig. 8 of Hippler et al. [20] and Fig. 11 of Kappel et al. [21]). Above approximately 1000–1100 K the rate coefficient undergoes a sudden drop-off within a small temperature window, after which the rate increases sharply again with increasing temperature. This peculiar temperature dependence cannot be captured by the sum of two modified Arrhenius expression as was previously attempted [10]. However capturing this temperature dependence was found to be crucial to the prediction of the current experimental data. Although the rate coefficient is probably better parameterized by a non-Arrhenius expression, here we employed the following expression:

$$k_{15} = 1.41 \times 10^{18} T^{-1.76} e^{-30/T} \\ + 1.12 \times 10^{85} T^{-22.3} e^{-13538/T} \\ + 5.37 \times 10^{70} T^{-16.72} e^{-16558/T} \\ + 1.0 \times 10^{136} T^{-40} e^{-17514/T} \\ + 2.51 \times 10^{12} T^2 e^{-20131/T}$$

to account for the peculiar temperature dependence as close as possible, using rate data from a large number of studies [20–28] and over the 298–1600 K temperature range (see Figure S1 attached in the supplementary information). The CHEMKIN suite of programs can employ this form of the rate expression. The current expression produces rate constants for k_{15} that range from 1.66×10^{13} to $5.81 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ over the temperature range 1200–1700 K which is consistent with recent direct measurements in a shock tube by Srinivasan et al. [29] who recommend rate coefficients $(3.01 \pm 1.81) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

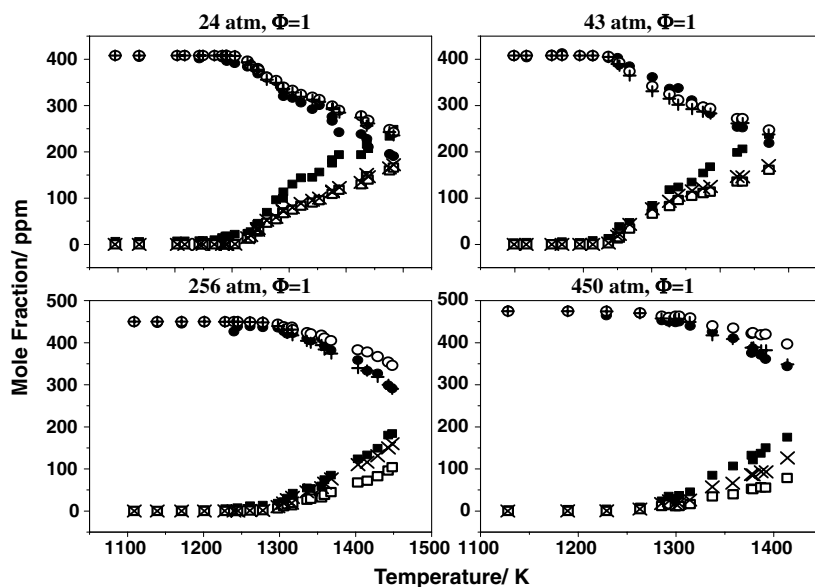


Fig. 7. [●], Expt. CO; [■], Expt. CO₂; [○], base model CO; [□], base model CO₂; [⊕], revised base model CO; [⊗], revised base model CO₂.

Figure 7 shows that with this single rate revision the revised Davis et al. [10] or revised base model can accurately predict the shock tube data for the entire pressure range of 24–450 atm. The predictive quality of the base model against datasets presented in [10] is basically unaffected by the revision of the k_{15} expression.

The agreement between experiments and model is certainly encouraging considering the potential for non-ideal gas behavior at 450 atm. Under this condition the real-gas equation of state deviates from the ideal gas equation by about 7%. A consideration of the non-ideal gas behavior led to a minimal effect on the model predictions in line with a recent detailed evaluation of the effects of non-ideal gas behaviour in the HPST [30]. The effect of the non-ideal gas behavior on the equilibrium constants of three-body reactions was also analyzed. Again sensitivity tests show little to no effect on model predictions.

Lastly, it is interesting to note that the mean free path under a nominal pressure of 450 atm is $<10 \text{ \AA}$, yet the ability of the base model (with the revision made for k_{15}) to reconcile all of the data shown here suggest that the caging effect, which would otherwise affect the elementary reaction rate coefficient at excessively high pressures, is unimportant here.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.proci.2006.08.057](https://doi.org/10.1016/j.proci.2006.08.057).

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Comments

Marcos Chaos, Princeton University, USA. Unlike the previous talk in this session [1], your analysis does not identify $\text{CO} + \text{HO}_2$ as one of the sensitive reactions. This is intriguing. We show in upcoming work [2] that under highly dilute mixture conditions, such as in your case, kinetic sensitivity may differ and reactions participating during the induction period have considerable effect in the system. This may explain your results.

The rate of $\text{HO}_2 + \text{OH}$ is fitted using the data from Hippler et al. [3] which show a minimum near 1200 K. New data from Kappel et al. [4] indicate a minimum near 1000 K. Due to the rapid increase of the $\text{HO}_2 + \text{OH}$ rate at high temperatures, fitting either set of data would lead to significantly different rate values for $T > 1000$ K which would have a direct effect on the modeling of the data presented ($1000 < T < 1500$ K). Why did the authors choose to fit the older data set?

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Reply. The sensitivity analysis does not identify $\text{CO} + \text{HO}_2$ to be important at our experimental conditions simply because of the low rate coefficient adopted for this channel based on the Princeton Flow Reactor experiments ([9] in paper). There are significant uncertainties for the rate coefficient for this reaction as highlighted in the earlier talk ([1] in comment). As mentioned in our article, one could adopt the Tsang and Hampson ([19] in paper) recommendation (higher by an order of magnitude than the Davis et al. recommendation) to reconcile the differences between the model and experiment at high pressures. However, this would worsen the predictions of the flow reactor measurements. Furthermore, the conclusion and analysis of the earlier talk suggests a revision of this rate coefficient further downward on the basis of recent RCM ignition delay experiments. More recent, high-level quantum chemistry calculation and master equation analysis support the notion of a lower rate value for $\text{CO} + \text{HO}_2$ [2]. Consequently, it appears that under our conditions high pressures and $T > 1200$ K this reaction will not play a significant role.

The direct measurements for the rate coefficient for the $\text{OH} + \text{HO}_2$ reaction show an intriguing trend with a deep narrow minimum at T from 1000 to 1200 K based on the Kappel et al. or the Hippler et al. experiments respectively. On the other hand, recent measurements ([29] in paper) spanning T from 1200 to 1700 K do not show any temperature effect with a constant value of $(5 \pm 3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}$. It is impossible to reconcile all the direct measurements with a single

expression; however, the fitted rate expression lies within the quoted experimental uncertainties for the rate coefficient at high temperatures and also provides a good fit to our experimental data.

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Joe Michael, Argonne National Lab, USA. Regarding OH+HO₂, you developed an expression to explain the rate behavior between room temperature and 1700–1800 K showing the deep minimum at 1000 K found by Troe and coworkers. Your experiments were from 1100 to 1400 K, so is it not true that you used rate constants between 4 and 8×10^{-11} cm³ molecule⁻¹s in agreement with our recent determination?

Reply. We were aware of your recent work ([29] in paper) on the direct measurement of the rate coefficient for OH + HO₂ = H₂O + O₂. As you had pointed out,

the modified rate expression for this reaction gives rate coefficients that range from 3.0×10^{-11} to 9.6×10^{-11} cm³ molecule⁻¹s in the *T* range from 1200 to 1700 K in line with your measurements.

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David M. Golden, Stanford University, USA. When changing the Davis mechanism, or any other mechanism that has been created by optimization, you should really find other targets and reoptimize.

Reply. The revision to the model does not affect the predictions to any of the other 36 targets against which the model was optimized. The current experiments (spanning a previously unexplored *P–T* regime) served to revise this model and extend it further to a wider range of *T* and *P* conditions thereby making it more comprehensive.