Inhibition of Premixed Carbon Monoxide–Hydrogen–Oxygen–Nitrogen Flames by Iron Pentacarbonyl†

MARC D. RUMMINGER† AND GREGORY T. LINTERIS*

Building and Fire Research Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

This paper presents measurements of the burning velocity of premixed CO–H₂–O₂–N₂ flames with and without the inhibitor Fe(CO)₅ over a range of initial H₂ and O₂ mole fractions. A numerical model is used to simulate the flame inhibition using a gas-phase chemical mechanism. For the uninhibited flames, predictions of burning velocity are excellent and for the inhibited flames, the qualitative agreement is good. The agreement depends strongly on the rate of the CO + OH ↔ CO₂ + H reaction and the rates of several key iron reactions in catalytic H- and O-atom scavenging cycles. Most of the chemical inhibition occurs through a catalytic cycle that converts O atoms into O₂ molecules. This O-atom cycle is not important in methane flames. The H-atom cycle that causes most of the radical scavenging in the methane flames is also active in CO–H₂ flames, but is of secondary importance. To vary the role of the H- and O-atom radical pools, the experiments and calculations are performed over a range of oxygen and hydrogen mole fraction. The degree of inhibition is shown to be related to the fraction of the net H- and O-atom destruction through the iron species catalytic cycles. The O-atom cycle saturates at a relatively low inhibitor mole fraction (~100 ppm), whereas the H-atom cycle saturates at a much higher inhibitor mole fraction (~400 ppm). The calculations reinforce the previously suggested idea that catalytic cycle saturation effects may limit the achievable degree of chemical inhibition. Published by Elsevier Science Inc.

INTRODUCTION

The production of the effective and widely used fire suppressant CF₃Br and other related compounds has been banned due to their contribution to ozone depletion. Currently, there exists no replacement fire suppressant with all of the desirable properties of CF₃Br, and the search for alternative compounds has intensified. It is well established that some metallic compounds are very powerful flame inhibitors [1–5]. The compound iron pentacarbonyl, Fe(CO)₅, has been found to be up to two orders of magnitude more effective than bromine-containing compounds at reducing the burning velocity of premixed hydrocarbon–air flames [1, 6]. Although Fe(CO)₅ is toxic and flammable, understanding its inhibition mechanism could provide insight into the behavior of other highly effective agents and aid in the development of new nontoxic agents.

In recent years, several detailed studies of Fe(CO)₅ have been undertaken. Reinelt and Linteris [7] studied the flame inhibition effect of iron pentacarbonyl in methane–oxygen–nitrogen mixtures by measuring the burning velocity of premixed flames and the extinction strain rate of counterflow diffusion flames. The experiments showed that for small amounts of Fe(CO)₅ the effect was roughly linear, but above a certain loading the effect was nearly independent of the Fe(CO)₅ concentration. The authors postulated that the decreasing inhibition was due to loss of active gas-phase species through condensation. Rumminger et al. [8] developed a chemical mechanism for Fe(CO)₅ inhibition of methane–oxygen–nitrogen flames, and through numerical simulations concluded that the inhibition occurs primarily through gas-phase chemistry. Flame simulations using the chemical mechanism in Ref. 8 showed promising agreement between model and experiment. The mechanism successfully predicted the trends for various equivalence ratios and oxygen mole fractions; however, the authors had increased the rates of several key
reactions\(^1\) (within experimental uncertainty) to improve quantitative agreement, and consequently recommended additional testing and refinement of the mechanism.

In the present paper we examine the effect of Fe(CO)\(_5\) in CO–H\(_2\)–O\(_2\)–N\(_2\) flames, which have a different radical pool than the methane flames of previous studies. Calculations of uninhibited premixed flame structure indicate that the peak mole fraction of O atom is four times higher in stoichiometric CO–H\(_2\)–air flames (containing between 0.2 and 1.0% H\(_2\)) than a stoichiometric CH\(_4\)–air flame, whereas the concentrations of H-atom and OH are between 1.5 and 7 times lower. These differences permit examination of the effect of radical pool composition on inhibition. Since previous calculations\(^2\) have shown that inhibition in methane flames occurs primarily from radical recombination cycles involving H atoms, it is of interest to determine if other mechanisms are important in flames with reduced H-atom mole fraction. In CO flames the H-atom mole fraction can be adjusted by varying the amount of H\(_2\) in the reactant mixture. Finally, the numerical calculations in methane-air flames indicated that above a certain loading chemical inhibitors can lose their effectiveness because the radical pool has already been lowered to equilibrium levels. By varying the radical pool size, CO flames can be used to investigate whether the observed saturation in the effectiveness of iron pentacarbonyl is due to condensation or radical pool depletion.

The oxidation mechanism of CO has fewer reactions than those of hydrocarbon fuels, allowing easier isolation of the important inhibition reactions. For this reason, many researchers have used CO flames in studies of halogen inhibition [9–16]. The simplicity of the CO system has additional significance in the present work. In previous studies with methane flames, the rates of key inhibition reactions suggested by Jensen and Jones [17] were increased in order to accurately match the observed burning velocity reductions. It is of interest here to determine if the faster rates are necessary for modeling moist CO flames—which are chemically much closer to the rich H\(_2\)–O\(_2\) flames used by Jensen and Jones (reactions of iron-containing species with hydrocarbons are not presently included in the mechanism). Finally, carbon monoxide flames are relevant to fire research since CO is a dominant intermediate species in hydrocarbon flames and its oxidation is often the rate-limiting step in product formation.

The approach in the present research is to determine the effect of Fe(CO)\(_5\) on the overall reaction rate of premixed flames. The laminar burning velocity is a widely used measure of the effectiveness of chemical inhibitors, and allows straightforward comparison with the numerically calculated flame structure, providing useful insight into the mechanism of inhibition.

Our study of flame inhibition is intended to provide an understanding of flame suppression. Although the processes have different end points (weakening the flame vs. extinguishing it), the underlying mechanism is similar: the agent reduces the overall reaction rate of the fuel–air mixture. Inhibition can be viewed as an early stage of suppression in which the inhibitor weakens the flame, making it more vulnerable to extinction by external factors such as heat loss or fluid-mechanical instability. Inhibition—and eventually suppression—occurs as the agent reduces the rate of heat release of the flame. For chemically acting agents, the agent interferes with the reactions that consume the fuel and intermediates. Hence, we can study the effect of small agent concentrations on flame chemistry and build chemical kinetic models that describe the effect of the agent on the combustion reactions. By using laboratory-scale premixed and diffusion flames that are amenable to modeling, we can validate the chemical kinetic model and gain insight into which processes are most important. Later, we can continue to construct and refine the mechanism for higher inhibitor concentrations and for flames and fuels that are more representative of fires. Finally, an understanding of the modes of action of effective agents such as Fe(CO)\(_5\) can lead researchers to chemicals that have similar favorable proper-

---

\(^1\)The reactions and increased rates were FeO + H\(_2\)O \(\leftrightarrow\) Fe(OH)\(_2\) \(k_1 = 1.62\times 10^9\) s\(^{-1}\) \(+\) 13, increased by 3\(\times\)), FeOH + H \(\leftrightarrow\) FeO + H\(_2\) \(k_2 = 1.50\times 10^9\) s\(^{-1}\) \(+\) 14 exp(\(-805/T\)) \(+\) 14, increased by 5\(\times\)), Fe(OH)\(_2\) + H \(\leftrightarrow\) FeOH + H\(_2\)O \(k_3 = 1.98\times 10^9\) s\(^{-1}\) \(+\) 14 exp(\(-302/T\)) \(+\) 14, increased by 3\(\times\)).

\(^2\)To avoid excessive repetition, references to previous calculations of Fe(CO)\(_5\)-inhibited methane flames refer to Ref. 8 unless otherwise noted.
ties, while avoiding characteristics such as diminishing effectiveness at high concentration.

In addition to the flame inhibition experiments and modeling, we present measurements of the burning velocity of uninhibited CO–H₂–O₂–N₂ flames with varying amounts of H₂, and compare the measurements with calculations. Although there are numerous measurements of CO flame speed in the literature [9, 18–21], there is a lack of data for near-stoichiometric CO–H₂–O₂–N₂ flames with H₂ mole fractions between 1.50·10⁻⁴ and 2.0·10⁻².

In the remainder of the paper, we describe the experimental technique, the numerical calculation procedure, and the results for uninhibited and inhibited CO–H₂–O₂–N₂ flames. We interpret the chemical kinetics of the inhibiting iron species in CO flames, comparing them with results for CH₄ flames, and analyze how changing oxygen or hydrogen content affects the flame inhibition.

**EXPERIMENTAL**

**Premixed Flame System**

A Mache-Hebra nozzle burner (inner diameter 1.02 ± 0.005 cm) [22] with a schlieren imaging system [23] is used to measure the average burning velocity with the total area method [24]. The burner produces straight-sided schlieren and visible images which are very closely parallel. Gas flows are measured with digitally controlled mass flow controllers (Sierra Model 860)³ with a quoted repeatability of 0.2% and accuracy of 1% of full-scale flow, which have been calibrated with bubble (Gillian Gilibrator) and dry (American Meter Co. DTM-200A) flow meters so that their accuracy is 1% of indicated flow. The fuel gas is carbon monoxide (Matheson UHP, 99.9% CO, with the sum of CH₄ and H₂O < 10 ppm) and hydrogen (Matheson UHP, 99.999% H₂, with sum of N₂, O₂, CO₂, CO, Ar, CH₄, and H₂O < 10 ppm); the oxidizer stream consists of nitrogen (boil-off from liquid N₂) and oxygen (MI Industries, H₂O < 50 ppm, total hydrocarbons < 5 ppm). The experimental arrangement has been described in detail previously [25] and the optical and image processing systems have been refined as described below.

Inhibitor is added to the flame by diverting part of the nitrogen stream to a two-stage saturator maintained in an ice bath at 0°C. The diverted gas (less than 8% of the total flow) bubbles through liquid Fe(CO)₅ before returning to the main nitrogen flow, and is assumed to be saturated with Fe(CO)₅ vapor. Although the saturator is the same as used previously, the assumption of saturation has been verified by flowing the Fe(CO)₅-laden gases into a condensation coil immersed in a −60°C alcohol bath. After a specified elapsed time, the ends of the coil were capped and the weight gain of the coil [i.e., the amount of Fe(CO)₅] was measured. After performing the condensation experiment for several carrier-gas flow rates, a linear fit of the data was generated to quantify the dependence of Fe(CO)₅ concentration on carrier-gas flow rate. The experimental results and theoretical prediction based on carrier-gas saturation were within 5% of each other across a wide range of flow rates.

The schlieren image of the flame is used to represent the flame surface. An optical system (a white-light source with a vertical slit at its exit, lenses, a vertical band, and filters) generates the schlieren image of the flame for capture by a 776 × 512 pixel CID array (Cidtec CID371OD). The image is digitized by a 640 × 480 pixel frame-grabber board (Data Translation 3155) in a Pentium-II computer. The images are acquired and written to disk using the free UTHSCSA ImageTool program [26]. For each flame condition, 10 images are collected at a rate of one per second. The flame area is determined (assuming axial symmetry) using custom image-processing software. Finally, the burning velocity is calculated by dividing the volumetric flow rate (corrected to 1 atmosphere and 298 K) by the average flame area for the 10 images.

In these experiments, the low rate of heat loss to the burner, the low strain rate, and the low curvature facilitate comparisons of the burning
Measured and Calculated Burning Velocity of Uninhibited Stoichiometric CO–H₂–O₂–N₂ Flames with Varying Oxygen Content and Varying Hydrogen Content

<table>
<thead>
<tr>
<th>( X_{O_2,ox} )</th>
<th>( X_{H_2} )</th>
<th>( v_{o,exp} ) (cm/s)</th>
<th>( v_{o,num} ) (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.183</td>
<td>0.01</td>
<td>32.7 ± 0.8</td>
<td>30.5</td>
</tr>
<tr>
<td>0.21</td>
<td>0.01</td>
<td>39.6 ± 1.1</td>
<td>35.8</td>
</tr>
<tr>
<td>0.24</td>
<td>0.002</td>
<td>25.1 ± 0.6</td>
<td>22.3</td>
</tr>
<tr>
<td>0.24</td>
<td>0.005</td>
<td>36.2 ± 0.9</td>
<td>31.2</td>
</tr>
<tr>
<td>0.24</td>
<td>0.01</td>
<td>46.2 ± 1.4</td>
<td>41.1</td>
</tr>
<tr>
<td>0.24</td>
<td>0.015</td>
<td>59.0 ± 2.4</td>
<td>48.7</td>
</tr>
</tbody>
</table>

The primary sources of uncertainty in the average burning velocity measurement are (1) accuracy of the flow controllers, (2) measurement of ambient pressure and temperature, (3) determination of the flame area, (4) the effect of flame base location on flame area, (5) the location of the schlieren image relative to the cold gas boundary. The relative uncertainty for burning velocity measurements ranges between 3% and 6.5%, and between 1% and 4.5% for normalized burning velocity. In general, uncertainty increases with increasing burning velocity. The tables of burning velocity assign uncertainty to each measurement of uninhibited burning velocity. The expanded relative uncertainties for parameters related to the accuracy of the flow controllers are as follows: 1.4% for equivalence ratio; and 1.1%, 1.2%, and 6.5% for the inlet reactant mole fractions of \( O_2 \), \( H_2 \), and \( Fe(CO)_5 \), respectively. For the latter, we use a vapor pressure correlation from Ref. 30 (which does not report an uncertainty). Based on the manufacturer's analysis of the bottled gases, the estimated background hydrogen in the reactant stream is less than 75 ppm.

NUMERICAL MODEL

One-dimensional freely propagating premixed flames are simulated using the Sandia flame code Premix [31], the Chemkin subroutines [32], and the transport property subroutines [33]. For all of the calculations the absolute tolerance is \( 10^{-14} \), the relative tolerance is \( 10^{-9} \), GRAD is 0.20, and CURV is 0.35. Thermal diffusion (Soret effect) is included in the calculations. Solutions typically contain between 85 and 130 grid points. The initial temperature is 298 K and the pressure is 1 atmosphere. The kinetic mechanism and thermodynamic data of Yetter et al. [34] (13 species and 37 chemical reactions) serve as a basis for describing moist carbon monoxide oxidation. Note that we use the modified Arrhenius rate for \( CO + OH \leftrightarrow CO_2 + H \) from Baulch et al. [35] because numerical calculations indicated that most of the CO oxidation was occurring below 2000 K (temperature above which a different rate expression was recommended [34]). Iron pentacarbonyl is added to the unburned CO–H₂–
RESULTS AND DISCUSSION

O₃-N₂ mixture at mole fractions of up to 500 ppm. The chemical mechanism for Fe(CO)₅ inhibition of flames (12 species and 55 reactions) and necessary thermodynamic and transport data are compiled from a variety of sources as described in Ref. 8. It should be emphasized that the reaction mechanism used for the present calculations should be considered only as a starting point. Numerous changes to both the rates and the reactions incorporated may be made once a variety of experimental and theoretical data are available for testing the mechanism.

Uninhibited Flames

Figure 1 shows the measured burning velocities for CO-H₂-air flames with varying amounts of hydrogen (for the reader's convenience, the data are also presented in tabular form in Table 2). We were not able to obtain a steady flame for hydrogen mole fractions (X_H₂) below 0.0024 or above 0.014. If extrapolated to hydrogen-free conditions, our measurements would agree reasonably well with the measurements of Palmer and Seery [9], who used the cone frustum method (reported measurement uncertainty of ±10%) to measure the burning velocity of CO-air flames with 45-150 ppm of H₂.

Figure 1 also shows the calculated burning velocity using the mechanism from Ref. 34 with several different sets of rate constants for CO + OH → CO₂ + H [35-38]. Table 3 lists calculated forward rate constants for each formulation at several temperatures. The 1992 rate expression of Baulch et al. [37] yields a burning velocity about 20% higher than the experiments, while the remaining three rate expressions predict values less than 10% lower than the experiments. Since there is a relatively large uncertainty in the rate of CO + OH near 2000 K [39], adjustment of this rate to match the present data seems unwarranted.

Examination of the numerical results shows that the CO + OH reaction is important even at very low hydrogen concentration. At X_H₂ = 0.001, 70% of the CO oxidation proceeds through CO + OH, while 28% of the CO oxidation proceeds through CO + O + M. At X_H₂ = 0.015 the split is 88% through CO + OH and 10% through CO + O + M.

Inhibited Flames

Effect of O₂ Mole Fraction

Figure 2 presents measurements (symbols) and calculations (lines) of the burning velocity of Fe(CO)₅-inhibited CO-H₂-O₂-N₂ flames with varying amounts of oxygen. As previously seen for CH₄-air flames inhibited by Fe(CO)₅, inhibition is strongest in the flames with the lowest X_O₂,O₂ (the oxygen mole fraction in the oxidizer prior to mixing with the fuel). The experimental results show that inhibition is proportional to inhibitor concentration at low inhibitor mole fraction (X_in), but after a certain concentration,
### TABLE 3
Comparison of the Rates for CO + OH ⇌ CO₂ + H Used in Figure 1a

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>b</th>
<th>(E_a/R)</th>
<th>(k_f)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1000</td>
</tr>
<tr>
<td>Baulch et al. (1973) [35]</td>
<td>1.50E + 07</td>
<td>1.3</td>
<td>-385</td>
<td>1.75E + 11</td>
</tr>
<tr>
<td>Baulch et al. (1992) [37]</td>
<td>3.25E + 10</td>
<td>1.5</td>
<td>-250</td>
<td>2.57E + 11</td>
</tr>
<tr>
<td>Woolridge et al. [36]</td>
<td>2.12E + 12</td>
<td>0</td>
<td>2630</td>
<td>1.53E + 11</td>
</tr>
<tr>
<td>Yu et al. [36]</td>
<td>4.4E + 06</td>
<td>1.547</td>
<td>67</td>
<td>1.89E + 11</td>
</tr>
<tr>
<td>Wooldridge et al. [38]</td>
<td>2.12E + 12</td>
<td>0</td>
<td>2630</td>
<td>1.53E + 11</td>
</tr>
</tbody>
</table>

a The rate expression and the forward rate \(k_f = A T^b \exp\left(-\frac{E_a}{RT}\right)\) at several temperatures are presented. Units for \(k\) are \(\text{cm} \cdot \text{mole} \cdot \text{s}\).

Additional Fe(CO)₅ has little effect on the burning velocity. A plausible (but untested) explanation is that particle formation removes the inhibiting species at high inhibitor loading [7]. The experimental results in Fig. 2 support this suggestion: as the flame temperature increases, the leveling-off point shifts to higher Fe(CO)₅ mole fraction.

Changing the oxygen mole fraction of the uninhibited CO flames changes several features which may affect the burning velocity reduction caused by added Fe(CO)₅. Table 4 lists the peak temperature and peak mole fraction of O, H, and OH in uninhibited flames with \(X_{O2,ax}\) equal to 0.183, 0.21, and 0.24. Raising the oxygen mole fraction over this range increases the final temperature by 209 K and the peak radical mole fractions by 30% to 60%. Although several variables are changing simultaneously, it is reasonable to expect the hotter flames, with their larger radical pool, to be affected less by a fixed quantity of Fe(CO)₅, yielding the smaller slope in Fig. 2. (A detailed analysis of the effect of \(X_{O2,ax}\) is undertaken later in this paper.)

The calculated normalized burning velocities (shown by the lines in Fig. 2) reproduce the trend of greater inhibition at lower \(X_{O2,ax}\) for low \(X_{in}\) and predict a reduced marginal effect as more inhibitor is added. At low values of \(X_{in}\), the slopes of the predicted normalized burning velocity curves are reasonably close to the measured slopes, but above about 100 ppm the measured and calculated normalized burning velocities diverge, with the model failing to reproduce the leveling off and overpredicting the inhibition effect. Nonetheless, we can use the numerical results at low inhibitor mole fraction to understand the reasons for the greater inhibition at lower \(X_{O2,ax}\), as well as other features. Further, results at higher values of \(X_{in}\) can be used to investigate the relevant gas-phase chemistry predicted by the model if there was not a loss of the active species to a condensed phase.

### TABLE 4
Calculated Maximum Mole Fraction and Superequilibrium Mole Fraction of O, H, and OH, and Maximum Temperature for Three Different \(X_{O2,ax}\) for the Uninhibited Flames of Fig. 2

<table>
<thead>
<tr>
<th>(X_{O2,ax})</th>
<th>(X_{O,max})</th>
<th>(X_{H,max})</th>
<th>(X_{OH,max})</th>
<th>(X_{O,max} - X_{O,eq})</th>
<th>(X_{H,max} - X_{H,eq})</th>
<th>(X_{OH,max} - X_{OH,eq})</th>
<th>(T_{max}) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.183</td>
<td>0.011</td>
<td>0.0045</td>
<td>0.0024</td>
<td>0.01</td>
<td>0.0043</td>
<td>0.00097</td>
<td>2262</td>
</tr>
<tr>
<td>0.21</td>
<td>0.014</td>
<td>0.0052</td>
<td>0.0029</td>
<td>0.015</td>
<td>0.0049</td>
<td>0.00095</td>
<td>2376</td>
</tr>
<tr>
<td>0.24</td>
<td>0.018</td>
<td>0.0058</td>
<td>0.0035</td>
<td>0.015</td>
<td>0.0054</td>
<td>0.00084</td>
<td>2471</td>
</tr>
</tbody>
</table>

![Fig. 2. Measured and calculated inhibition effect of Fe(CO)₅ for various O₂ concentrations in stoichiometric CO-H₂-O₂-N₂ flames with \(X_{H₂} = 0.01\).](image-url)
The information obtained from flame speed measurements is global, and many reactions in the mechanism can affect the results. Nonetheless, a comparison of the measured and predicted burning velocities together with investigation of the numerical results can be used to identify key reactions for further investigation. In previous work with methane flames, the rates of the dominant inhibition reactions (those in the H-atom cycle recommended by Jensen and Jones [17]) were increased (within experimental uncertainty) to better predict the experimental results. In Fig. 2, the model shows slightly more inhibition for $X_{\text{O}_2,\text{ox}} = 0.24$ than the experiments. While it is tempting to use the present data to move the rates of the H-atom cycle back in the direction of the original recommendations [17], it is premature to do so. The excessive inhibition only occurs for one case; also, the effect of reaction rates in the fuel oxidation mechanism (exclusive of the inhibition mechanism) must be considered, as will be described below. Based on these considerations, we use the increased rates for the H-atom cycle reactions for the analyses in the present paper.

As described in a preceding section and Fig. 1, for uninhibited CO flames, the rate of the reaction CO + OH has a large effect on the burning velocity predicted by the numerical calculation. For inhibited flames, the rates of the key inhibition steps obviously have a large effect on model performance. However, the rate selected for the CO + OH reaction also affects the degree of predicted inhibition by Fe(CO)$_5$. Figure 3 shows the combined effect of differing rates for the CO + OH reaction and for the reactions in the H-atom cycle [8]. The measured and predicted normalized burning velocities as a function of the mole fraction of Fe(CO)$_5$ are shown for two values of the CO + OH rate and for the fast and slow rates for the H-atom recombination cycle. As the figure shows, the selection of the appropriate rates for the inhibition reactions depends upon selection of the CO + OH rate.

For the remainder of this paper, we use the 1973 Baulch et al. [35] CO + OH rate recommended by Yetter et al. [34] and the faster rates for the H-atom cycle reactions from Ref. 8. As illustrated in the NIST Chemical Kinetics Database [39], there is large uncertainty in the rate of CO + OH near 1800 K. Although the rate of Yu et al. [36] provides better agreement with our experimental data (Fig. 1), we retain the 1973 Baulch et al. [35] rate since it has been extensively tested against a variety of experimental data from flames, flow reactors, and shock tubes [34]. For the inhibition reactions, the premixed methane flame results suggest use of the faster rates for the H-atom cycle. In Fig. 3, considering only the region of low $X_{\text{in}}$, the results are ambiguous, although with the two rates for CO + OH, the faster rates for the cycle (solid lines) bracket the experimental data, while the slower rates for the cycle (dotted lines) lie predominantly outside the data. Also, the recent measurements of Rollason and Plane [40] for the reaction FeO + H$_2$O + He(N$_2$) $\leftrightarrow$ Fe(OH)$_2$ + He(N$_2$), which is part of the H-atom cycle, argue for a rate even higher than that suggested in Ref. 8. Note that while the absolute magnitude of the predicted inhibition is affected by the rates selected for the H-atom cycle, the qualitative behavior is not, and the conclusions of this paper are unaffected by these rates.

**Catalytic Inhibition Cycles**

In previous research on bromine-containing species [41, 42], conversion of radicals (e.g., H) into less reactive species (e.g., H$_2$) has been found to be the dominant mode of action for
chemical inhibitors and suppressants. A similar H-atom catalytic cycle involving iron oxide and hydroxide intermediates has been found to be important in CH₄-O₂-N₂ flames inhibited by Fe(CO)₅ [8]. Reaction pathway and sensitivity analyses for the inhibited CO flames reveals that the H-atom catalytic cycle is active. A new finding, however, is that there is an additional catalytic cycle which scavenges O atoms and which is much more important than the H-atom cycle for CO flames. The appearance of O-atom scavenging is consistent with the high peak O-atom mole fraction of the present flames as compared to H or OH (Table 4), and the finding that O-atom trapping is important for fluorinated-species inhibition of CO flames [16]. Recent computations of the thermochemistry of iron compounds at flame conditions support the possibility of multiple radical recombination cycles [43]. O-atom recombination by iron compounds has been reported previously [44] for flow tube experiments in which Fe(CO)₅ was added to the reactant gases. Removal of O-atom by CF₃Br in a flow tube has also been reported [45]. These previous studies, however, did not propose a catalytic cycle for O-atom recombination.

The reactions that comprise the catalytic O-atom scavenging cycle are

\[
\begin{align*}
Fe + O_2 + M &\leftrightarrow FeO_2 + M \quad (R1) \\
FeO_2 + O &\leftrightarrow FeO + O_2 \quad (R2) \\
FeO + O &\leftrightarrow Fe + O_2 \quad (R3) \\
O + O &\leftrightarrow O_2.
\end{align*}
\]

The first and third reactions in the cycle have been studied in the laboratory. The rate for (R1) has been measured by several researchers [46, 47], and the rate for (R3) has been measured by Fontijn et al. [48]. The rate for second reaction was estimated [8], lowering its rate reduces the calculated inhibition and improves agreement with the present experiments.

The primary reaction pathways for iron species are shown in Fig. 4, where both the H- and O-atom catalytic cycles are illustrated. Fe(CO)₅ decomposition occurs through several steps in which the CO ligands are sequentially removed (for simplicity, these steps are not shown in the figure), leaving Fe. The Fe is converted first to FeO₂ and then to FeO. A portion of the FeO is converted back to Fe, thus completing the O-atom cycle; the remainder of the FeO participates in the H-atom cycle.

Although the reactions (R1)-(R3) were present in the inhibition mechanism, a significant contribution from the O-atom cycle was not found in the studies of CH₄-O₂-N₂ flames. Instead, reactions (R1)-(R2) converted Fe to one of the species in the main inhibition cycle (FeO), and (R3) was a minor reaction. The authors found that most of the radical scavenging for methane flames occurs through the H-atom catalytic cycle.

Part of the effect of the catalytic cycles illustrated in Fig. 4 is a suppression of radical super-equilibrium. Figure 5 shows the calculated O-atom mole fraction as a function of position in stoichiometric CO-H₂-air flames with X_{H₂} = 0.01 and various X_{O₂}. As the inhibitor mole fraction increases, the peak mole fraction decreases; and perhaps more important, the amount of super-equilibrium decreases, providing fewer radicals to support flame propagation. The H-atom superequilibrium also decreases, partially through catalytic scavenging, and partially as a result of the fast O, H, and OH shuffle reactions.

**Saturation of Catalytic Cycles**

Returning to the results in Fig. 2, we examine why the inhibition decreases as X_{O₂,ox} increases using the technique of reaction flux analysis.
INHIBITION OF CO FLAMES BY IRON PENTACARBONYL

The flux of a species though a particular reaction is defined as the integral of the reaction rate over the domain of interest (here taken to be the cold boundary to the time of peak radical mole fraction). The total flux of a species is the sum of fluxes from each reaction, and the fractional flux is the flux of interest divided by the total. We measure the relative importance of the iron reactions by calculating the fractions of H-atom and O-atom consumption that occur through the most important iron reactions. For the H-atom, the following reactions are considered: Fe(OH)$_2$ + H $\leftrightarrow$ FeOH + H$_2$O, FeOH + H $\leftrightarrow$ FeO + H$_2$, and FeO + H$_2$O $\leftrightarrow$ Fe(OH)$_2$. For the O-atom, the following reactions are considered: Fe + O$_2$(+ M) $\leftrightarrow$ FeO$_2$(+ M), FeO$_2$ + O $\leftrightarrow$ FeO + O$_2$, FeO + O $\leftrightarrow$ Fe + O$_2$, FeOH + O + M $\leftrightarrow$ FeOOH + M. These are the reactions in the cycles of Fig. 4; previous modeling results and analysis using the graphical postprocessor Xsenkplot [49] have shown them to be the most important inhibition reactions.

Figure 6 shows the fraction of H-atom and O-atom flux through the catalytic cycles for three different values of $X_{O2,ox}$. At low $X_{in}$, the fractional flux is inversely related to $X_{O2,ox}$. As $X_{O2,ox}$ decreases, stronger inhibition may be caused by the larger fraction of H atoms (and to a lesser extent, O atoms) scavenged through the catalytic cycles. The inhibition cycles essentially compete with the chain branching reactions, and hence reduce the overall reaction rate. While most of the inhibition appears to result from recombination of O atoms, the reaction flux results imply that the difference in behavior at low and high $X_{O2,ox}$ is due to the increasing importance of the H-atom cycle at low $X_{O2,ox}$.

The diminished effectiveness of Fe(CO)$_5$ at high $X_{in}$ may be explained, in part, by the behavior illustrated in Fig. 6. Above 100–200 ppm of Fe(CO)$_5$, the O-atom cycle saturates. That is, increasing $X_{in}$ does not lead to a greater fraction of the radicals being recombined by the iron species. The H-atom cycle saturates at values of $X_{in}$ only slightly higher. The saturation explains why the calculated curves in Fig. 2 have decreasing slopes as $X_{in}$ increases. It is of interest to note that inhibition caused by Fe(CO)$_5$ diminishes more rapidly in CO flames than CH$_4$ flames. Part of the reason may be due to the importance of the O-atom cycle for CO flames and the rapid saturation of this cycle relative to the H-atom cycle. These explanations are obtained from the calculated results; while saturation might conceivably occur in the actual flames, it should be emphasized that the experiments show an even greater loss of effectiveness, and the modeling and experimental results do not agree well at higher values of $X_{in}$. The discrepancy has been attributed to loss of inhibiting species through condensation [7].

The saturation of catalytic cycles again suggests the existence of limits to chemical inhibition, as was previously shown for an idealized inhibitor [50]; a similar saturation was shown for fluoromethanes, which trap H-atoms noncata-
lytically [51]. Although Fe(CO)$_5$ may have the confounding effect of condensation, the finding of catalytic cycle saturation has practical implications for fire suppressant design. For example, a blend of noncondensing chemical fire suppressants might be used to rapidly drop the radical mole fractions, but the performance of such a blend could be limited by catalytic cycle saturation. To produce effective blends, it may be advantageous to combine catalytic agents with those that lower the equilibrium mole fraction of radicals, either thermally or chemically [52, 53].

To further explore the importance of the various reactions, we calculate first-order sensitivity coefficients of the burning velocity to the reaction rates [31, 54]. Figure 7 shows the sensitivity coefficients for the three different values of $X_{O_2,ox}$ with 50 ppm of Fe(CO)$_5$. The calculations show that among the reactions in the iron mechanism, the reactions in the O-atom and H-atom catalytic cycles are most important for reducing burning velocity. As the oxygen concentration increases, the sensitivity coefficients of the reactions in the catalytic cycles decrease.

**Effect of H$_2$ Mole Fraction**

When $X_{O_2,ox}$ is changed, the radical pool and flame temperature are affected. Since the inhibitor behavior is affected by both of these variables, it is desirable to change the radical pool without changing the temperature. In CO flames, this can be accomplished by varying $X_{H_2}$. Within the limits set by our experimental apparatus, we were able to stabilize CO flames with $X_{H_2}$ of 0.002, 0.005, 0.01, and 0.015. An elevated oxygen content relative to air (24% O$_2$/76% N$_2$) was necessary to achieve this range. Below $X_{H_2} = 0.002$ the flame would not stabilize at a height of 13 mm; above $X_{H_2} = 0.015$ the flame oscillated too much for accurate measurement. Table 5 lists calculated maximum mole fraction and amount of superequilibrium for O, H, and OH for CH$_4$-air and CO-H$_2$-O$_2$-N$_2$ flames with varying $X_{H_2}$. As the table shows, the variation of $X_{H_2}$ results in a change in maximum H-atom and OH mole fraction of about a factor of 3.5 (approximately linearly with $X_{H_2}$), and little change in maximum O-atom mole fraction. Note also that the O-atom superequilibrium is approximately constant with $X_{H_2}$, but that H-
TABLE 5
Calculated Maximum O, H, and OH Mole Fraction and Superequilibrium; Maximum Temperature; for Calculated Burning Velocity for Four Different Values of $X_{H_2}$

<table>
<thead>
<tr>
<th>$X_{H_2}$</th>
<th>0.002</th>
<th>0.005</th>
<th>0.01</th>
<th>0.015</th>
<th>CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{O,max}$</td>
<td>0.018</td>
<td>0.018</td>
<td>0.018</td>
<td>0.017</td>
<td>0.0044</td>
</tr>
<tr>
<td>$X_{H,max}$</td>
<td>0.002</td>
<td>0.0037</td>
<td>0.0058</td>
<td>0.0074</td>
<td>0.0085</td>
</tr>
<tr>
<td>$X_{OH,max}$</td>
<td>0.0014</td>
<td>0.0024</td>
<td>0.0035</td>
<td>0.0044</td>
<td>0.011</td>
</tr>
<tr>
<td>$X_{O,max}-X_{O,eq}$</td>
<td>0.016</td>
<td>0.016</td>
<td>0.015</td>
<td>0.015</td>
<td>0.0037</td>
</tr>
<tr>
<td>$X_{H,max}-X_{H,eq}$</td>
<td>0.0018</td>
<td>0.0034</td>
<td>0.0054</td>
<td>0.0068</td>
<td>0.0076</td>
</tr>
<tr>
<td>$X_{OH,max}-X_{OH,eq}$</td>
<td>0.00024</td>
<td>0.0005</td>
<td>0.00084</td>
<td>0.00111</td>
<td>0.0049</td>
</tr>
<tr>
<td>$T_{max}$ (K)</td>
<td>2471</td>
<td>2468</td>
<td>2471</td>
<td>2475</td>
<td>2353</td>
</tr>
<tr>
<td>$v_{o,num}$ (cm/s)</td>
<td>22.3</td>
<td>31.2</td>
<td>41.1</td>
<td>48.7</td>
<td>55.6</td>
</tr>
</tbody>
</table>

* Also shown for comparison are the same parameters for a CH$_4$-O$_2$-N$_2$ flame. ($X_{O_2,eq}$ = 0.24 and $\phi$ = 1 for all flames shown.)

atom and OH superequilibrium increases as $X_{H_2}$ increases.

Comparing the CO flames with a CH$_4$ flame, several features stand out: (1) the maximum O-atom mole fraction is about four times higher in the CO flames, (2) the H-atom mole fraction is lower in the CO flames (but is approaching the CH$_4$ value as $X_{H_2}$ increases), (3) the maximum OH concentration is 3 to 8 times lower in the CO flames. These differences allow testing and study of the inhibition mechanism under significantly different flame conditions.

Figure 8 shows the effect of Fe(CO)$_5$ on flames with different levels of H$_2$ in the reactants and $X_{O_2,eq}$ = 0.24. For reference, experimentally determined normalized burning velocities for CH$_4$-air flames [7] are also shown. (The slight discontinuity in the $X_{H_2}$ = 0.015 data ("x" symbols) between $X_{in}$ = 150 and 250 ppm occurs because mass flow controllers with slightly different calibrations were used for the low $X_{in}$ and high $X_{in}$ measurements.) Compared to methane flames, the effect of small amounts of Fe(CO)$_5$ in CO-H$_2$ flames is weaker for $X_{H_2}$ = 0.01 and 0.015, about equal for $X_{H_2}$ = 0.005, and stronger for $X_{H_2}$ = 0.002 (note that the $X_{H_2}$ = 0.002 flame was not stable for $X_{in}$ > 50 ppm). A significant finding is that the CH$_4$ curve shows linear behavior longer than the CO curves, resulting in a lower normalized burning velocity at high Fe(CO)$_5$. This is surprising since the reduced effect at high $X_{in}$ is believed to be due primarily to condensation of iron species. One would expect less condensation in the 120 K hotter CO flames, and therefore a strong inhibition effect to higher $X_{in}$. The opposite behavior indicated in Fig. 8 implies that saturation of the catalytic cycles may be the dominant cause for reduced effectiveness, or perhaps that the degree of iron-species condensation is increased in the slower CO flames.

Numerical calculations have been performed for the moist CO flames with varying $X_{H_2}$, and Fig. 9 compares the calculations with measurements of normalized burning velocity. Similar to the predictions for varying $X_{O_2,eq}$ (Fig. 2), at low Fe(CO)$_5$ mole fraction (< 100 ppm), the mechanism reasonably predicts the magnitude of inhibition and dependence on $X_{H_2}$ (although the
predicted inhibition is too strong for higher values of \( X_{H_2} \). In addition, the leveling off is not predicted and there is little difference between the calculations at different \( X_{H_2} \), other than the varying initial slopes; that is, the point where diminishing effectiveness starts is not predicted by the mechanism.

Figure 10 presents the fractional H- and O-atom destruction from the iron species catalytic cycles. The fractional amount of O-atom scavenging is highest in flames with low \( X_{H_2} \), explaining why the hydrogen-deficient flames are inhibited more strongly at low \( X_{H_2} \). For \( X_{H_2} \) above 100 ppm, the fraction of O-atoms consumed through the iron reactions is around 0.85 for \( X_{H_2} = 0.002 \), but only 0.55 for \( X_{H_2} = 0.015 \). Figure 10 shows (as does Fig. 6) that the O-atom cycle saturates at a lower Fe(CO)\(_5\) mole fraction than the H-atom cycle. The importance of the O-atom cycle in CO flames and its more complete saturation may be one of the reasons that the normalized burning velocity levels off at a higher value in the CO flames than the CH\(_4\) flame.

Sensitivity coefficients of the burning velocity to selected reaction rates were also calculated for flames with 50 ppm of Fe(CO)\(_5\), and varying \( X_{H_2} \). At low hydrogen content the O-atom cycle reactions have the highest sensitivities, but as \( X_{H_2} \) increases, their sensitivity coefficients decrease. As \( X_{H_2} \) increases, the regeneration step (FeO + H\(_2\)O) in the H-atom cycle becomes more important, while the other two reactions become less important.

We also measured normalized burning velocity for rich (\( \phi = 1.2 \)) and lean (\( \phi = 0.8 \)) CO–H\(_2\) flames with \( X_{H_2} = 0.01 \), and found that inhibition is slightly stronger for lean flames than for rich flames. As in the case of CH\(_4\) flames, the dependence on \( \phi \) is weak.

**CONCLUSIONS**

In this paper we have presented measurements of the burning velocity of CO–H\(_2–O_2–N_2\) flames with and without the inhibitor Fe(CO)\(_5\) over a range of initial H\(_2\) and O\(_2\) mole fractions. The inhibited flames had four different H\(_2\) concentrations, and three different O\(_2\) concentrations. A numerical model was used to simulate the flame inhibition using a gas-phase chemical mechanism. Based on the experiments and calculations, we reach the following conclusions:

For *uninhibited* flames, experimental burning velocities are within 10% of the results of calculations using the mechanism from Yetter et al. [34] for several different rates of the CO + OH \( \leftrightarrow \) CO\(_2\) + H reaction. Calculated burning velocities using the rate of Yu et al. [36] agree closely with our data, whereas those using the 1992 recommendation of rate from Baulch et al. [37] are significantly higher than the measurements.

For *inhibited* flames, the calculations and experiments show good qualitative agreement. The degree of quantitative agreement depends strongly on the rates of the CO + OH \( \leftrightarrow \) CO\(_2\) +
INHIBITION OF CO FLAMES BY IRON PENTACARBONYL

H reaction, the reactions in the H-atom cycle, and the FeO₂ + O ↔ FeO + O₂ reaction.

Most of the chemical inhibition occurs through a catalytic recombination cycle that converts O atoms into O₂ molecules. This cycle was not found to be important in the previous numerical study of methane flames. The H-atom cycle that caused most of the radical scavenging in the methane flames is also active in the CO flames described here, but is of secondary importance.

Based on reaction flux analyses, the degree of inhibition by Fe(CO)₅ is shown to be related to the fraction of the total O- and H-atom destruction which is attributable to iron species reactions.

In the calculated results, the O-atom cycle saturates at a relatively low inhibitor mole fraction (~100 ppm), whereas the H-atom cycle saturates at a much higher inhibitor mole fraction (~400 ppm). The earlier saturation of O-atom cycle compared to the H-atom cycle could be a reason why the CO flames have higher normalized burning velocity than CH₄ flames at high Fe(CO)₅ mole fraction.

There are several practical implications for the suppression of hydrocarbon flames from the present work. Depending upon the hydrogen content of the fuel, the catalytic recombination of O atom may be as important as catalytic recombination of H atom and should be considered. Catalytically acting agents (singly or in blends) may be useful only up to a certain mole fraction; above that value, additional agent may prove far less effective. Finally, if elimination of radical superequilibrium is readily achieved by catalytically acting agents, further reduction in overall reaction rate may require additives that lower the equilibrium values of radicals, either thermally or chemically.

The inhibition mechanism qualitatively reproduces the dependence of flame inhibition on hydrogen and oxygen concentration at low inhibitor loading, but several questions remain unanswered. The most critical one is why the normalized burning velocity levels off as the Fe(CO)₅ concentration increases. Because the leveling-off point changes with varying X_H₂, but the flame temperature does not change, there is less reason to believe that condensation is the cause; results in the present paper imply that saturation of the catalytic cycles may be important. While both radical saturation and iron species condensation are likely operative, it is not possible with the present data to separate the effects. Hence, there is an even greater need for measurements of particles in flames inhibited by Fe(CO)₅ in order to understand the reason for the loss of effectiveness of this very powerful flame inhibitor. Of course, measurement of the rates of key iron reactions, especially the reactions in the catalytic cycles, is also an important area for future work.

We are grateful to undergraduate student researcher Nikki Prive for assistance with data acquisition and uncertainty analysis programs, and Dr. Rich Yetter for discussion of the chemical kinetics of CO oxidation.

REFERENCES

15. Fallon, G. S., Chelliah, H. K., and Linteris, G. T., *Twenty-Sixth Symposium (International) on Combust-
26. Image Tool is a free Windows 95-based program developed at the University of Texas Health Science Center at San Antonio, Texas and available from the Internet by anonymous FIP from ftp://maxrad6.uthscsa.edu or http://ddsdx.uthscsa.edu


Received 30 March 1999; revised 28 July 1999; accepted 11 August 1999