

FLAME INHIBITION BY FERROCENE, ALONE AND WITH CO₂ AND CF₃H

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INTRODUCTION

Iron pentacarbonyl (Fe(CO)₅) is an extraordinarily effective flame inhibitor, up to two orders of magnitude more efficient than CF₃Br at reducing the burning velocity of premixed flames [1-3]. Recent progress has been made in understanding its mechanism of inhibition [4-7]. However, it is flammable and highly toxic, and addition at mole fractions above a few hundred ppm* does not result in further flame speed reduction. If other non-toxic forms of iron exist, which are also superb inhibitors and which maintain their action up to higher mole fractions, they could lead to the development of very effective fire suppressants.

Previous research has shown that iron atom in the gas phase leads to the inhibiting iron-species intermediates, and that the main property required for the parent molecule is that it readily decomposes at flame temperatures to release iron atom. A possible alternative source of Fe is ferrocene (Fe(C₅H₅)₂ or Fecj. Ferrocene modifies the sooting tendency of flames [8-13], is added to materials as a flame retardant [14], is an antiknock agent, and is used as a source of iron atoms for kinetic studies. It is also far less toxic than Fe(CO)₅.

In this work we present the first measurements of flame inhibition by ferrocene, and compare its performance with that of Fe(CO)₅ and CF₃Br in the same flames. We numerically model Fec's flame inhibition using the iron-species mechanism developed for studies of Fe(CO)₅ flame inhibition. Finally, we present results on the performance of Fec in combination with other agents, including CO₂, and CF₃H. The present research demonstrates that the efficiency of Fe(CO)₅ is not unique and that there are methods for overcoming its loss of performance. (More details of the work can be found in Linteris et al.[15].)

Flame inhibition by highly effective chemical inhibitors has been described in the literature. The inhibition is characterized by several gas-phase radical recombination cycles that proceed at nearly gas-collisional rates. It has been shown that radical recombination on particle surfaces is not likely to be fast enough to produce the observed burning velocity reductions at low inhibitor mole fraction [7]. Particle formation *is* important, however, in that condensation serves as a loss mechanism for the active inhibiting species when their concentration is above the saturation vapor pressure. Additionally, at high enough inhibitor mole fractions, a loss in effectiveness is expected for *all* catalytic inhibitors since eventually, radical concentrations are lowered to equilibrium levels, and further reduction is not possible. For Fe(CO)₅ however, the loss in effectiveness caused by condensation occurs well before any approach to equilibrium of radicals.

Although the present tests are performed in premixed flames of methane, they are relevant to the suppression of practical fires. Methane oxidation is atypical of that of larger hydrocarbons; however, Babushok and Tsang have recently observed [16] that for a wide variety of hydrocarbons, including methane, the burning velocity is most sensitive to the rates of the same reactions. Since these reactions are the ones most influenced by an inhibitor, the trends in inhibitor effec-

In the present paper, all references to percent or ppm are on a volume basis.

tiveness are the same for most hydrocarbons. As has been discussed previously [6], burning velocity measurements are an important first step in assessing an inhibitor's effectiveness and testing mechanism performance. In future research, it is desirable to test these highly effective agents in flames more closely resembling actual fires.

EXPERIMENT

The flame speed S_L provides a measure of an agent's reduction of the global reaction rate. The experimental arrangement, described in detail previously [4, 6, 17], has been modified to accommodate a new evaporator for ferrocene and heating of the gas lines and burner tube [15]. A Mache-Hebra nozzle burner (1.0 cm \pm 0.05 cm diameter) produces a premixed Bunsen-type flame about 1.3 cm tall with a straight-sided schlieren image that is captured by a video frame-grabber board in a PC. Digital mass flow controllers hold the oxygen mole fraction in the oxidizer stream X_{O_2, O_x} , the equivalence ratio ϕ , and the flame height constant while maintaining the inlet mole fraction of the inhibitor (X_i) at the desired value. The average burning velocity is determined from the reactant flows and the schlieren image using the total area method. The fuel gas is methane (Matheson* UHP, 99.9%), and the oxidizer stream consists of nitrogen (boil-off from liquid N₂) and oxygen (MG Industries, H₂O < 50 ppm, and total hydrocarbons < 5 ppm). The inhibitors used are Fec (Aldrich), Fe(CO)₅ (Aldrich), CF₃H (DuPont), CF₃Br (Great Lakes), N₂, and CO₂ (Airgas). The Fe(CO)₅ is added to N₂ carrier gas using a two-stage saturator in an ice bath. Because the vapor pressure of Fec is much lower than that of iron pentacarbonyl, Fec addition at mole fractions up to 650 ppm requires both higher bath temperature (79.1 °C held within 0.1 °C) and higher nitrogen carrier gas flow rates (up to 2800 cm³/min) relative to Fe(CO)₅. Also, the solid state of Fec requires an evaporator with larger surface areas for heat and mass transfer. Our evaporator design, based upon that of Megaridis [9], has a (30 \pm 5) cm³ packed bed (to provide the bulk α the ferrocene), followed by 30 sublimation stages (to ensure that the carrier gas is saturated with Fec at the bath temperature). Each sublimation stage consists of a 5-mm layer of ferrocene on a 2.36 cm diameter 60-mesh stainless steel screen. A 4-mm gap separates each stage. The vapor pressure correlation of Pelino et al. [18] is used to determine the ferrocene mole fraction in the carrier gas. Temperature controllers maintain the transfer lines at (80 \pm 3) °C and the burner tube at (80 \pm 1) °C. For all flames, the equivalence ratio (in the absence of inhibitor) is 1.0, and agent mole fraction is calculated relative to the total reactant flow. The flows of fuel, oxidizer, Fec-N₂, and the blended agent (CO₂, or CF₃H) are mixed after the Fec evaporator. The inlet reactant stream temperature is (80 \pm 1) °C, which corresponds to a calculated adiabatic flame temperature of 2260 K and 2391 K for uninhibited flames at X_{O_2, O_x} =0.21 and 0.244.

NUMERICAL MODELING

The laboratory flames inhibited by Fec and Fec-CO₂ blends were numerically modeled as one-dimensional freely-propagating flames. Solutions were obtained using the Sandia flame code *Premix* [19], and the *Chemkin* [20] and transport property [21] subroutines. Details of the calculations are provided elsewhere [15]. Little is known about the chemical kinetic behavior of

* Certain commercial equipment, instruments, or materials are identified in this paper to adequately specify the procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards & Technology, nor does it imply that the materials or equipment are necessarily the best available for the intended use.

ferrocene in flames. Rates exist for its thermal decomposition: $k = 2.188 \cdot 10^{16} \exp(-384 \text{ kJ}/RT) \text{ s}^{-1}$ [22], but the activation energy is high, leading one to suspect that reactions with radicals may also be important. Thermodynamic data are available [23, 24], and the transport properties are estimates [25, 26]. A reaction set for combustion of methane and larger hydrocarbon fragments was adopted from Sung et al. [27]. We added iron chemistry from a mechanism developed for flame inhibition by $\text{Fe}(\text{CO})_5$ [5]. Overall, the kinetic model contains 105 species and 677 reactions. Calculations showed that addition of C_5H_5 at mole fractions up to 400 ppm had a negligible effect on the burning velocity, and that the major effect of Fec is from the iron chemistry. 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.

RESULTS AND DISCUSSION

INHIBITION BY FERROCENE

Figure 1 shows the relative burning velocity reduction with addition of Fec (open symbols) or $\text{Fe}(\text{CO})_5$ (closed symbols) to the present slightly pre-heated (80°C) methane-air flames. (The uncertainties in the experimental data, described in detail previously [28], are typically about $\pm 5\%$.) Data are plotted as normalized burning velocity, which is the burning velocity of the inhibited flame divided by the value for the same flame in the absence of inhibitor. The uninhibited experimental burning velocities used for the normalizations are $(53.7 \pm 3) \text{ cm/s}$ and $(75.9 \pm 6) \text{ cm/s}$ for $X_{\text{O}_2, \text{O}_2} = 0.21$ and 0.244 respectively; for comparison, the calculations for uninhibited flames using GRI-Mech 1.2 yield 55.5 cm/s and 72.6 cm/s . The effect of the two agents is essentially the same, with very strong initial inhibition followed by a loss of effectiveness above a few hundred ppm of agent, as found previously for $\text{Fe}(\text{CO})_5$ inhibition in flames with reactants at 21°C [4].

Figure 1 shows that for both Fec and $\text{Fe}(\text{CO})_5$, the magnitude of the inhibition is strongly dependent upon the oxygen mole fraction in the oxidizer, with oxygen-deprived flames showing more rapid burning velocity reduction. As a result, blends of inert agents with iron-containing compounds may be particularly effective. The modeling results for the ferrocene-inhibited flames are also shown in Figure 1. The calculations (dotted lines) predict the flame speed reduction caused by ferrocene reasonably well. The major difference between the ferrocene reaction scheme and that for $\text{Fe}(\text{CO})_5$ is in the decomposition of the iron precursor. The present mechanism includes only the high-activation energy thermal decomposition step for Fec consumption: $\text{FeC}_{10}\text{H}_{10} \rightarrow \text{Fe} + 2 \text{C}_5\text{H}_5$, which has a peak reaction flux at 1800 K in the present flames. In contrast, iron pentacarbonyl decomposition has a peak reaction flux at about 900 K .

Figure 2 shows the normalized burning velocity for a methane-air flame with 400 ppm of ferrocene as a function of the activation energy E , of the one-step decomposition reaction. In the temperature range of the stoichiometric methane-air flame of the figure, the predicted inhibition effect of Fec is independent of the overall activation energy of the decomposition of Fec for values of E , less than about 400 kJ/mol . Hence, the decomposition rate of Fec used in the model

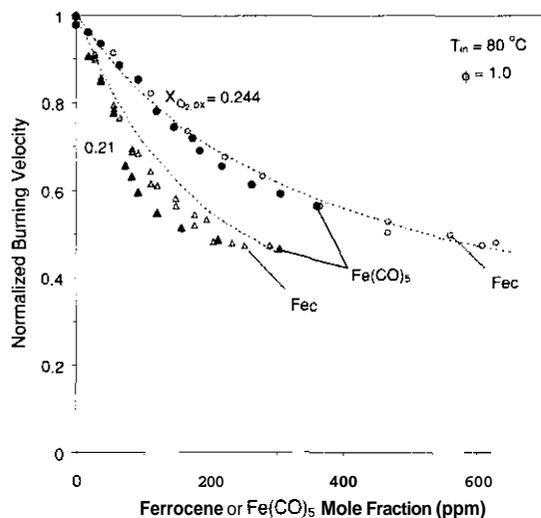


Figure 1. Normalized burning velocity of premixed $\text{CH}_4/\text{O}_2/\text{N}_2$ flames inhibited by ferrocene (open symbols) and $\text{Fe}(\text{CO})_5$ (closed symbols) for $X_{\text{O}_2,\text{Ox}} = 0.21$ and 0.244 , together with modeling predictions (dotted lines).

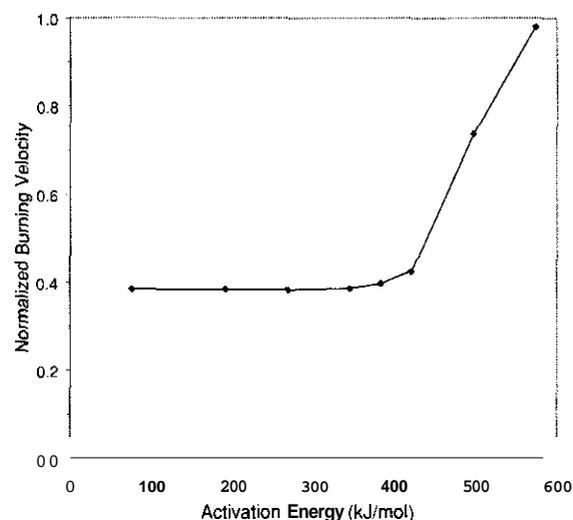
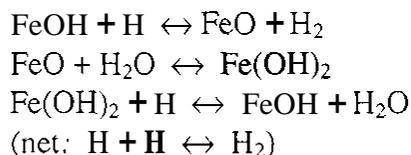


Figure 2. The normalized burning velocity of stoichiometric $\text{CH}_4/\text{O}_2/\text{N}_2$ flames at 400 ppm of Fec as a function of the activation energy of the one-step ferrocene decomposition reaction.

($E_a = 384 \text{ kJ/mol}$) does not influence the predicted behavior. For other conditions, however, (e.g., non-preheated reactants and highly diluted flames) the decomposition of Fec may need to be modeled more accurately to provide agreement with experimental data.

Since both the Fec and $\text{Fe}(\text{CO})_5$ mechanisms use the same iron sub-mechanism, the mode of flame speed reduction is similar. Decomposition of the ferrocene molecule releases iron atom in the gas phase. Iron reacts with O_2 to form FeO_2 , which reacts with O atom to form FeO . FeO is a long-lived intermediate, which together with $\text{Fe}(\text{OH})_2$ and FeOH , enters into the catalytic cycle for H -atom recombination:



The modeling results show that the stronger burning velocity reduction for the cooler flames ($X_{\text{O}_2,\text{Ox}} = 0.21$) is due to their smaller radical pool; in these flames, a given amount of iron can remove a larger *percentage* of the hydrogen radicals.

Ferrocene appears to be an alternative to the highly toxic iron pentacarbonyl for addition of gas-phase iron to a flame. Unfortunately, its effectiveness also appears to diminish as the mole fraction increases. For $\text{Fe}(\text{CO})_5$ the loss of effectiveness has been identified to be due to formation of condensed-phase particulates in the reaction zone [29]. Since addition of nitrogen clearly increases the rate of burning velocity reduction at low mole fraction (note the results in Figure 1 for $X_{\text{O}_2,\text{Ox}} = 0.21$ and 0.244), it is of interest to determine whether other thermally acting agents

can be combined with Fec to mitigate the loss of effectiveness. and perhaps enhance the flame speed reduction at low Fec mole fraction. It is desired to take advantage of the strong initial flame speed reduction from iron species in the flame, while avoiding the loss of active species due to condensation. A drawback, however. is that addition of an inert, while reducing the burning velocity, also increases the residence time for particle formation in the flume, so that condensation is increased [29]. It is not known a priori if the net effect of combining thermal and iron-containing agents will reduce the overall reaction rate faster than the increase of the rate of active-species condensation.

INHIBITION BY FERROCENE AND CO₂

Figure 3a and 3b present the experimental data for tests at $X_{O_2, O_N} = 0.21$ and 0.244. Data are shown for pure CO₂ as well as for CO₂-Fec blends corresponding to three values of the percentage of Fec in CO₂ (0, 0.25, and 1.5% in Figure 3a; 0, 0.4, and 1.5% in Figure 3b). For the pure compounds, addition of about 10% of CO₂ (or 25% N₂) reduces S_L by a factor of two at $X_{O_2, O_N} = 0.21$ or 0.244. Adding Fec to CO₂ produces a particularly effective agent. The equivalent of 0.35% Fec in CO₂ reduces the required CO₂ for a 50% reduction in the flame speed by about a factor of three at $X_{O_2, O_N} = 0.21$ and about a factor of two at $X_{O_2, O_N} = 0.244$. The combination of 1.5% Fec reduces the required CO₂ by ten (10), making this blend about as effective as CF₃Br (for which addition of about 1% halves the burning velocity). Nonetheless, the curvature in the ends of the data sets (particularly for 1.5% Fec in CO₂) illustrates condensation can be important. Although one might expect the slightly cooler, slower flames with added CO₂ to always show more condensation of iron species, the greater efficiency of the catalytic cycle in the diluted flames predominates for most of the conditions for the flame of Figure 3. Higher effectiveness of iron compounds in diluted flames has been observed previously for flames with X_{O_2, O_N} lowered below 0.21 [4].

The condensation behavior of the blends can be discerned from Figure 4a and 4b, which present additional data for CO₂ and ferrocene in stoichiometric flames with $X_{O_2, O_N} = 0.21$ and 0.244, respectively. In Figure 3, CO₂ and ferrocene were added together in proportional amounts, whereas in Figure 4, CO₂ is first added at a constant mole fraction (0, 2, and 6% in 4a; or 0, 4, and 12% in 4b), and then the Fec is added. This approach allows a clearer delineation of the effects of each component of the blend. As the figures show, the curve with 0% CO₂ (pure Fec) has a decreasing slope magnitude as X_{Fec} increases (due to increased condensation). For each of the other curves, the added CO₂ reduces the normalized burning velocity before the Fec is added, so that each curve starts at a value less than unity; addition of Fec further reduces the flame speed. Below an Fec mole fraction of about 70 ppm, the curves are all quite linear, showing that there is no loss of effectiveness. But for curves extending beyond this amount of Fec, there is increasing curvature as X_{Fec} increases (due to condensation). Nonetheless, at low mole fractions, the inhibition by Fec is actually stronger for conditions of higher CO₂ mole fraction (note the larger magnitude of the slope for the 12% CO₂ curve in Figure 4b). Hence, for some conditions, adding CO₂ makes Fec more effective. As discussed below, once the particles start to form, the deterioration of inhibition may be more rapid with added CO₂. These results imply that combinations of *non-condensing quantities* of several catalytic agents combined with a thermal agent can be particularly effective.

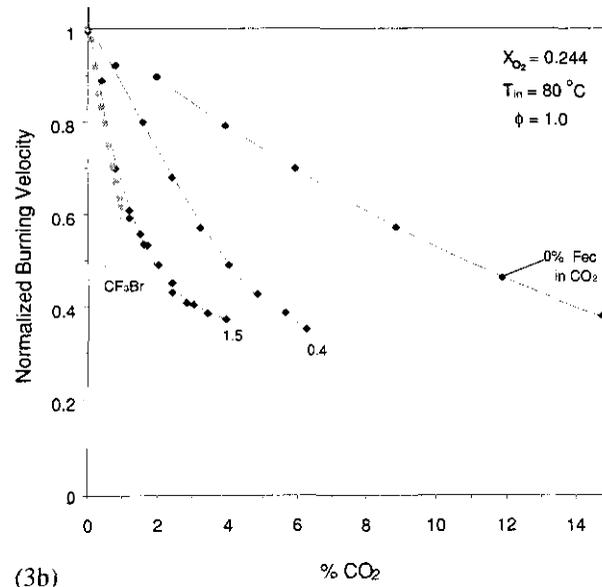
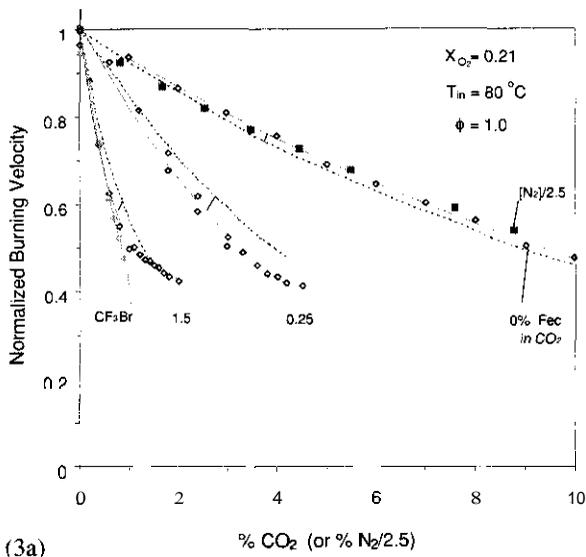


Figure 3. Normalized burning velocity of $\text{CH}_4/\text{O}_2/\text{N}_2$ flames, a) $X_{\text{O}_2, \text{O}_x} = 0.21$, b) $X_{\text{O}_2, \text{O}_x} = 0.244$, inhibited by CO_2 , by CO_2 -ferrocene blends, and by CF_3Br . The equivalent percentage of ferrocene in CO_2 (which is constant for each curve) is given. The solid lines are curve fits through the data, and the dotted lines, the calculated results. Data for nitrogen are included in (a) by dividing % N_2 by 2.5.

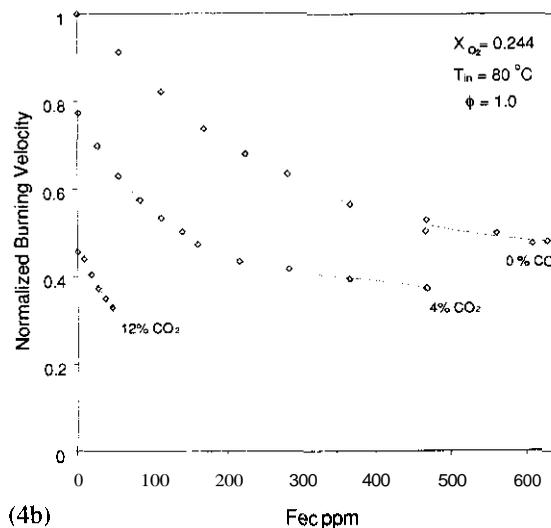
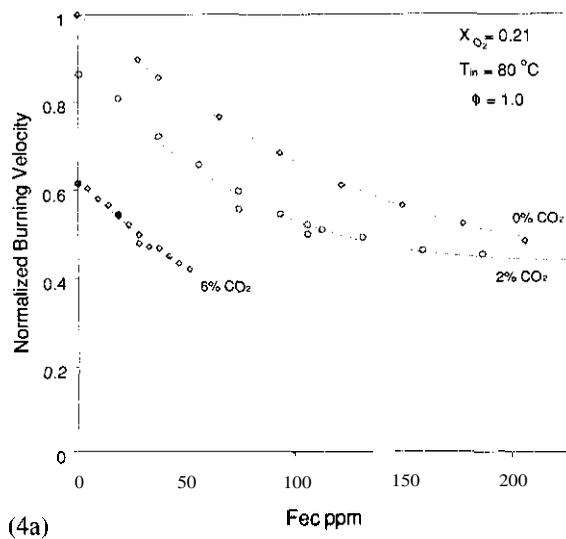


Figure 4. Normalized burning velocity of $\text{CH}_4/\text{N}_2/\text{O}_2$ flames, a.) $X_{\text{O}_2, \text{O}_x} = 0.21$, b.) $X_{\text{O}_2, \text{O}_x} = 0.244$, with 0, 2, and 6, or 0, 6, and 12 mole percent of CO_2 , respectively, added to the reactant stream, as a function of added ferrocene (lines are curve fits to the experimental data).

INHIBITION BY FERROCENE AND CF₃H

Many compounds are candidates for blending with catalytic agents, including thermally acting and other chemical agents. Hydrofluorocarbons, which are easily stored at moderate pressure, are of interest since they are presently used as halon replacements. These compounds have been found to reduce the burning velocity of premixed methane-air flames by (1) reducing *peak* H-atom mole fractions by acting as a sink for H atoms through reactions forming HF, and (2) lowering the temperature of the flame. Since they have also been shown to reduce the *equilibrium* mole fractions of radicals in flames lower than expected based on temperature reduction alone [30], they might be expected to show enhanced performance relative to CO₂ when combined with catalytic agents.

Figure 5 presents the burning velocity reduction caused by pure CF₃H addition to the above flames; a mole fraction of about 5% is required to reduce S_L by two. Data are also presented for addition of 0.35% Fec in CF₃H. Unlike ferrocene addition to CO₂, in which 0.35% Fec in CO₂ reduces the amount of CO₂ required by a factor of about five, this amount of ferrocene in CF₃H reduces the amount of CF₃H required only by about a third. This poor performance may be due to reactions between iron species and fluorine, which reduce the gas-phase mole fraction of the active iron-species intermediates, effectively poisoning the iron catalyst."

Since there presently exist no experimental data on the rates of reactions of iron species with fluorine containing species in flames, the poisoning effect of fluorinated hydrocarbons on iron-catalyzed radical recombination reactions is assessed through equilibrium calculations for the combustion products. The species included in the calculations are those in the mechanisms for hydrocarbon oxidation, iron-inhibition, and fluorinated hydrocarbon-inhibition [31], as well as the iron-fluorine species: FeF, FeF₂, FeF₃, Fe₂F₄, Fe₂F₆ [32]. Calculations were performed for the equilibrium products of a stoichiometric methane-air flame with 1% to 4% CF₃H containing 0.35% Fec (the conditions of Figure 5: see also Figure 6). The results of the calculations indicate that FeF and FeF₂ are major product species when CF₃H has been added. For 1% to 4% CF₃H, the amount of iron taken up by the sum of FeF and FeF₂ increases from 42 to 84%, making less iron available in the form of the active iron intermediate species Fe, FeO, FeOH, FeO₂, and Fe(OH)₂. The formation of fluorinated iron species with strong bonds can clearly act as a sink for iron in the flame, and reduce the mole fractions of active iron-containing species available to participate in the flame inhibition reactions. While the experiments and calculations are presented for CF₃H, the results are likely to be similar for larger HFCs such as C₂HF₅ and C₃HF₇ since the decomposition of all proceeds largely through the CF₃, CF₂, and CFO intermediates [17, 30, 33].

COMPARISON OF INDIVIDUAL AND BLENDED PERFORMANCE

The behavior of the blends of agents can be investigated by comparing the actual amount of flame speed reduction for the blend to the sum of the inhibition that would result from each agent individually. This approach is illustrated schematically in Figure 7. We adopt the inhibition index $\Phi(X_m)$ of Fristrom and Sawyer [34], where $\Phi(X_m) = \frac{(V_o - V(X_m))}{V_o} \left\{ \frac{X_{O_2, O_1}}{X_m} \right\}$ (and using the oxygen mole fraction in the oxidizer). The index $\Phi(X_m)$ is seen to be the magnitude of the average slope of the normalized burning velocity curve (times X_{O_2, O_1}) evaluated at the mole

* Tsang, W., personal communication, April 1999.

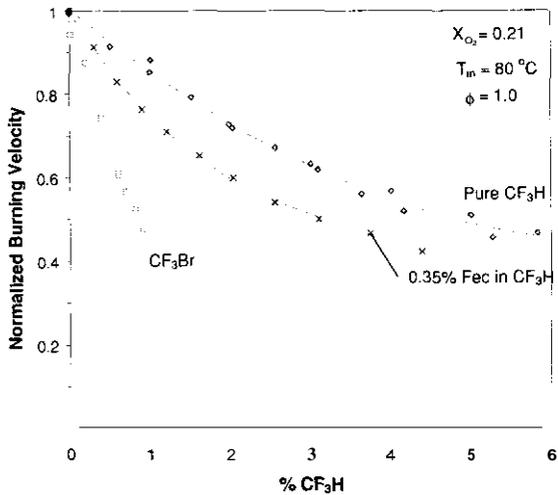


Figure 5. Normalized burning velocity of premixed $\text{CH}_4/\text{O}_2/\text{N}_2$ flames inhibited by pure CF_3H and by CF_3H with 0.35% ferrocene, together with data for CF_3Br . Lines are curve fits to the data.

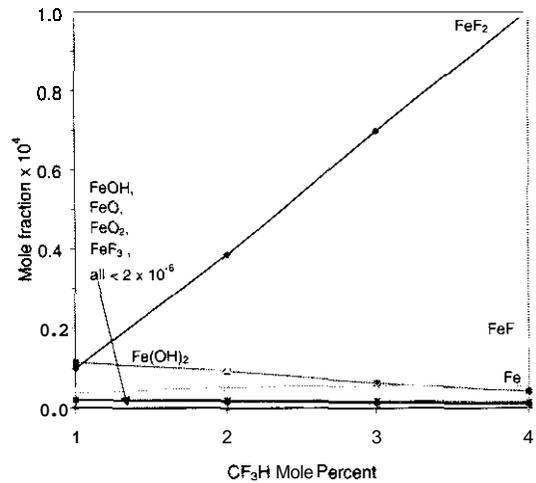


Figure 6. Equilibrium mole fraction of active inhibiting species (Fe , FeO , FeOH , $\text{Fe}(\text{OH})_2$) and iron-fluorine species with 1% to 4% CF_3H (containing 0.35% ferrocene) added to a stoichiometric methane-air reaction mixture.

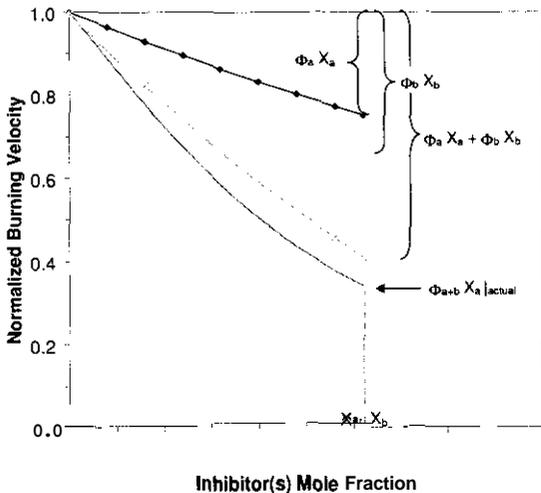


Figure 7. Illustration of linear contribution of burning velocity reduction from each component of a two-component blend of inhibitors, together with the actual reduction from the blend.

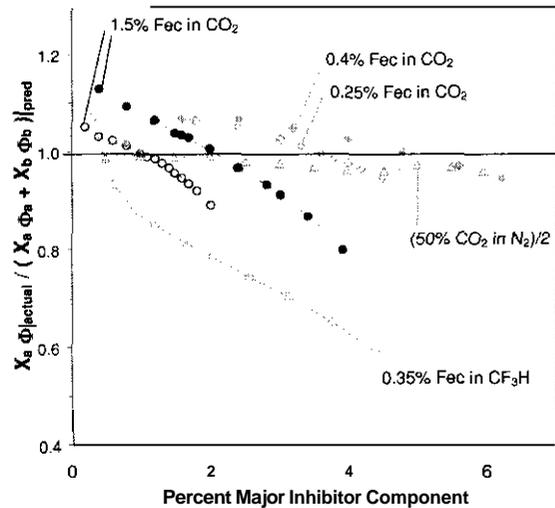


Figure 8. Ratio of the actual reduction in S_L from the two-component mix to the predicted reduction based on linear combination of the effect from each component. Open and closed symbols are for $X_{\text{O}_2, \text{O}_x} = 0.21$ and 0.244; lines are curve fits to the data. The percent CO_2/N_2 has been divided by two to fit on the figure.

fraction of interest X_{in} . For a given blend, we can evaluate the amount of normalized burning velocity *reduction* that would have been caused by each individual component of the blend, say components a and b . The predicted inhibition index is just a linear combination of the reduction from each component, or $X_a \cdot \Phi_{a+b}(X_a, X_b)|_{pred} = X_a \cdot \Phi_a(X_a) + X_b \cdot \Phi_b(X_b)$, in which a is the major component of the blend, (and we have selected it for defining $\Phi_{a+b}(X_a, X_b)$). The actual inhibition index $\Phi_{a+b}(X_a, X_b)|_{actual}$ is evaluated from the normalized flame speed of the blend (using X_a in its definition). The ratio of $X_a \cdot \Phi_{a+b}(X_a, X_b)|_{actual}$ to $X_a \cdot \Phi_a(X_a) + X_b \cdot \Phi_b(X_b)$ provides a reasonable indicator of the performance of the blend relative to the individual components.

As Figure 8 shows, a blend of CO_2 and N_2 (in the molar ratio of 1:2) provides a performance index of nearly 1.0 for N_2 added up to 12% (i.e., containing 6% CO_2). (The percent amount of the N_2/CO_2 mix plotted in Figure 8 is divided by two to allow plotting on the same scale.) In contrast, the poor performance of the Fec- CF_3H blend is clearly indicated by a decreasing performance index as X_{in} increases. For the CO_2/Fec blends, the combination appears to work slightly better than the individual components at low X_{in} of the blend, and slightly worse at higher X_{in} . The good performance at low X_{in} is due to the higher radical super-equilibrium that occurs with flame dilution as observed previously for N_2 addition [4]; the degraded performance at higher X_{in} is due to the longer residence times for condensation that result from the lower flame speeds [29]. In Figure 8, the condition at which the curves for Fec/ CO_2 cross over the unity ratio correspond roughly to the location on the curves in Figure 3, where the linear behavior has ended and the curvature begins.

CONCLUSIONS

We have presented the first data on flame inhibition by ferrocene and shown it to be as efficient as $\text{Fe}(\text{CO})_5$ at reducing the burning velocity of premixed methane flames. Ferrocene, like $\text{Fe}(\text{CO})_5$, loses its effectiveness at a mole fraction above a few hundred ppm. The experimental results are reasonably predicted by a gas-phase iron inhibition mechanism. The results imply that any rapidly decomposing iron-containing agent that releases atomic iron in the gas phase can act as a precursor for the active iron-species intermediates, and that the results are not unique to $\text{Fe}(\text{CO})_5$. As with $\text{Fe}(\text{CO})_5$, the magnitude of the inhibition by ferrocene has a strong dependence on the oxygen mole fraction. As a result, many combinations of CO_2 and Fec show strong inhibition, mitigating the loss of effectiveness observed for pure Fec or $\text{Fe}(\text{CO})_5$. The results imply that an inert agent, together with multiple catalytic agents (to keep the absolute mole fraction of each below the saturation point) may prove to be highly effective for all conditions. In contrast to the results with CO_2 , blends of CF_3H and Fec are not particularly effective, implying that iron species and halogens may enter into undesired reactions that poison the catalytic cycles. It means can be identified to introduce gas-phase iron compounds into fires safely, combinations of catalytically and relatively inert thermally acting inhibitors may prove to be an efficient approach for developing effective fire suppressants.

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