Flame Inhibition by Ferrocene, Carbon Dioxide, and Trifluoromethane Blends: Synergistic and Antagonistic Effects

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The production of CF_3Br has been banned. As a flame inhibitor, iron pentacarbonyl ($Fe(CO)_5$) is about two orders of magnitude more efficient than CF_3Br, but it is flammable and highly toxic, and its addition to premixed flames at mole fractions above a few hundred ppm does not further reduce the burning velocity. If other iron compounds can be identified which show the same strong inhibition but are less toxic and don't lose their effectiveness, they may find use in fire suppressants. Ferrocene ($Fe(C_5H_5)_2$ or Fec) modifies the sooting tendency of flames, is added to materials as a flame retardant and is an antiknock agent. It is far less toxic than $Fe(CO)_5$, and it may produce the same iron-containing intermediates. Here, we present the first measurements of flame inhibition by ferrocene, compare it with $Fe(CO)_5$ and CF_3Br, and present data showing how combining it with other compounds can overcome the loss in effectiveness experienced by both it and $Fe(CO)_5$.

Flame inhibition by bromine, alkali metals, and transition metals have been described in the literature, and their reduced effectiveness at higher mole fractions has been discussed in detail [1-3]. Since the chemicals are believed to act through homogeneous gas-phase catalytic radical recombination cycles, the inhibition mechanism requires a radical superequilibrium to be most effective. Consequently, once radicals are reduced to equilibrium levels via inhibitor addition, further reduction in the overall reaction rate from additional inhibitor is minimal. This loss in effectiveness due to radicals approaching their equilibrium values has been demonstrated for increasing mole fraction of inhibitor in calculations employing both an idealized "perfect" inhibitor [2] and $Fe(CO)_5$ [3], and has been discussed by Rosser et al. [4] and Hastie [5]. Nonetheless, the measured loss in effectiveness of $Fe(CO)_5$ occurs at a lower mole fraction than expected based on these calculations; the actual cause appears to be condensation of iron compounds and the resulting limit to the gas-phase iron-species concentrations [6]. Regardless of the cause of the loss of effectiveness, previous researchers [4,5,7-10] have suggested that combinations of thermally acting and catalytic agents might prove beneficial. The effectiveness of iron pentacarbonyl in premixed flames has been shown to be greatly increased at lower oxygen mole fraction, and the effect has been attributed to the larger superequilibrium ratio (the peak radical mole fraction divided by the equilibrium value) which exists at lower oxygen mole fraction [1]. In contrast, the effectiveness of relatively inert agents such as N_2 and CO_2 is not a strong function of the oxygen mole fraction in the oxidizer stream, $X_{O2,ox}$. (In the present work we find that addition of 10% CO_2 to flames with $X_{O2,ox}$ equal to either 0.21 or 0.244 reduces the normalized burning velocity by about half, whereas $Fe(CO)_5$ is more than twice as effective for $X_{O2,ox} = 0.21$ than for 0.244 [1]). Since adding a thermal agent raises the superequilibrium ratio, the possibility exists for very effective blends of catalytically and thermally acting agents. Consequently, we report here the burning velocity of premixed flames in the presence of combinations of a thermal agent CO_2, (which does not lose its effectiveness at higher mole fraction) and catalytic agents (which are superbly effective at low inhibitor mole fraction).

The premixed laminar flame speed S_L provides a measure of the effect of the inhibitor on the overall reaction rate. The experimental arrangement, described in detail previously [1,10,11], has been modified only to accommodate a new evaporator for ferrocene and heating of the gas lines and burner tube. 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 which is captured by a frame-grabber board in a PC. Digital mass flow controllers hold the equivalence ratio ϕ, $X_{O2,ox}$, and the flame height constant while maintaining the inlet mole fraction of the inhibitor X_{in} at the desired value. The inhibitors are N_2, CF_3H, CO_2, Fec, and $Fe(CO)_5$. The average burning velocity is determined from the reactant flows and the schlieren image using the total area method. As in earlier research, the fuel gas is

methane (Matheson[1] UHP, 99.9%), and the oxidizer stream consists of nitrogen (boil-off from liquid N_2) and oxygen (MG Industries, $H_2O < 50$ ppm, and total hydrocarbons < 5 ppm). The inhibitors used are Fec (Aldrich, 98%), $Fe(CO)_5$ (Aldrich), CF_3Br (Great Lakes), N_2, and CO_2 (Airgas). The $Fe(CO)_5$ is added to N_2 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 500 ppm requires both higher bath temperature (70 to 80 C, held within 0.01 C) and higher nitrogen carrier gas flow rates (up to 350 cm^3/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 [12], has a 30 ± 5 cm^3 packed bed (to provide the bulk of the ferrocene), followed by thirty sublimation stages (to insure that the carrier gas is saturated at the bath temperature); each stage consists of a 5 mm layer of ferrocene, 2.36 cm in diameter, on a 60 mesh stainless screen and a 4 mm gap. Temperature controllers maintain the transfer lines at 353 K $\pm$ 3 K and the burner tube at 353 K $\pm$ 1 K. For all flames, the equivalence ratio (in the absence of inhibitor) is 1.0, and agent mole fraction is calculated relative to the reactant total <u>without</u> the inhibitor.

The experimental burning velocity reduction caused by the addition of Fec and $Fe(CO)_5$ to the stoichiometric methane flames are presented in Figure 1. 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. (For Figs. 1 to 4, the solid lines are fits to the data.) As Figure 1 shows, Fec (closed symbols) reduces the burning velocity as effectively as does $Fe(CO)_5$ (open symbols), and it does not appear to lose its effectiveness until higher mole fraction. As with $Fe(CO)_5$, the magnitude of the inhibition is strongly dependent upon the oxygen mole fraction in the oxidizer, with oxygen-deprived flames inhibited much more strongly.

Figure 2 presents experimental data for addition of pure CO_2 (or pure N_2) and CO_2/Fec blends at four values of the equivalent percentage of Fec in CO_2: 0, 0.053%, 0.2%, and 0.54%. The last data point in a series represents the maximum value of X_{in} at which a flame could be stabilized. The blends of the inert and chemically acting agents are shown to be highly effective. Addition of about 10% of pure CO_2 (or 25% pure N_2) reduces S_L by a factor of two. Addition of the equivalent of 0.1% Fec to CO_2 reduces the required CO_2 by about a factor of two, and 0.6% Fec reduces the required CO_2 by ten, making this blend about as effective as CF_3Br (for which addition of about 1% halves the burning velocity). It is important to note that the flames with CO_2/Fec combinations in Figure 2 do not display the large loss in effectiveness, i.e. the plateau region, occurring in most of the curves in Figure 1. Although one might expect the slightly cooler, slower flames with added CO_2 to have more condensation of iron species, the greater efficiency of the catalytic cycle in the diluted flames predominates.

Other compounds may be convenient for blending with catalytic agents. Hydrofluorocarbons 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 reducing *peak* H-atom mole fractions through reactions forming HF and by 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 [13], they might be expected to show enhanced performance relative to CO_2 when combined with catalytic agents. Figure 3 presents the burning velocity reduction caused by pure CF_3H 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 the equivalent of 0.35% Fec in CF_3H. Unlike ferrocene addition to CO_2, in which 0.35% Fec in CO_2 reduces the amount of CO_2 required by a factor of about five, this amount of ferrocene in CF_3H reduces the amount of CF_3H required only by about 25%. 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 [5,14].

To further illustrate the synergistic behavior of Fec with CO_2 , and the antagonistic behavior of Fec with CF_3H, we examine the performance of the blend relative to individual contributions from each component. We define the normalized flame speed at each inhibitor mole fraction X_{in} as $N_{SL}(X_{in})$, and the reduction in the normalized

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[1] 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 and Technology, nor does it imply that the materials or equipment are necessarily the best available for the intended use.

flame speed as $R_{SL}(X_{in}) = 1 - N_{SL}(X_{in})$. Assuming that the flame speed reduction of a two-component blend $R_{SL}(X_{in})|_{blend}$ is a linear combination of the contribution from each component, $R_{SL}(X_{in,1}, X_{in,2})|_{blend} = X_{in,1}R_{SL,1} + X_{in,2}R_{SL,2}$, the predicted normalized burning velocity of the blend is $N_{SL}(X_{in,1},X_{in,2})|_{blend} = 1 - R_{SL}|_{blend}$. The ratio of the predicted to the actual normalized flame speed for several blends is shown in Figure 4. A value greater than unity shows that the blend provides a reduction in the normalized burning velocity more than expected based on a linear combination of the contribution from each component, while a value less than one shows the converse. In Figure 4, the curve near unity shows the result for a blend of 2/1 molar ratio of N_2 to CO_2; that is, for thermally acting agents in these flames and in this range of inhibitor mole fraction, the reduction in flame speed from CO_2 and N_2 is additive. As the figure shows, CO_2 with 0.54% Fec is significantly more effective than would be expected based on a linear combination of the performance of Fec and CO_2 alone, while CF_3H and Fec is significantly less effective than the sum of each individually.

We have presented the first data on ferrocene as a flame inhibitor, and shown it to be as efficient as $Fe(CO)_5$ at reducing the burning velocity of premixed methane flames. The results imply that either agent acts as an effective precursor for the active iron-species intermediates. For the data presented here, ferrocene does not appear to lose its effectiveness as drastically as does $Fe(CO)_5$, and its inhibition has just as strong a dependence on $X_{O2,ox}$. As a result, blends of CO_2 and Fec show very strong inhibition, overcoming the loss of effectiveness observed for pure Fec or $Fe(CO)_5$. Further, blends of CO_2 and Fec reduce the burning velocity of premixed methane-air flames more strongly than expected based on the performance of each individually. Blends of CF_3H and Fec, however, have been found to be much less effective than expected based on the performance of each individually, implying that iron species and halogens may enter into undesired reactions which poison the catalytic cycles. Nonetheless, if means can be identified to safely introduce gas-phase iron compounds into fires, combinations of catalytically and relatively inert thermally acting inhibitors may prove to be an efficient approach to solving a problem which threatens the global environment.

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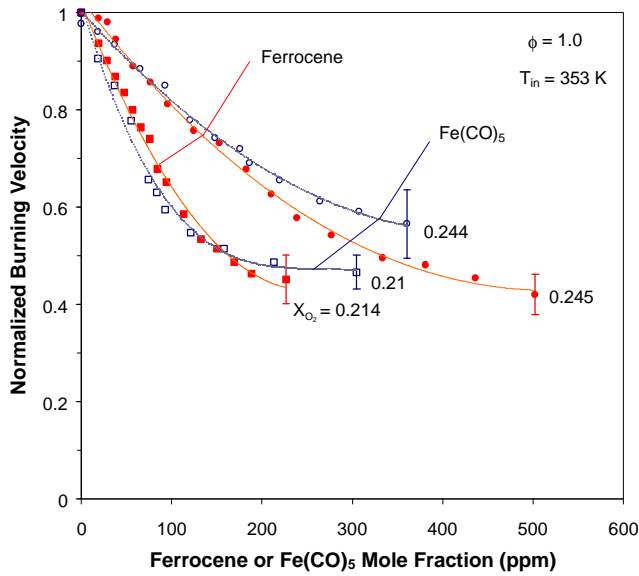[14]. Tsang, W., "Personal Communication, April 1999.

Figure 1 – Normalized burning velocity of premixed CH$_4$/O$_2$/N$_2$ inhibited by ferrocene and Fe(CO)$_5$ for several values of the oxygen mole fraction in the oxidizer $X_{O2,ox}$.
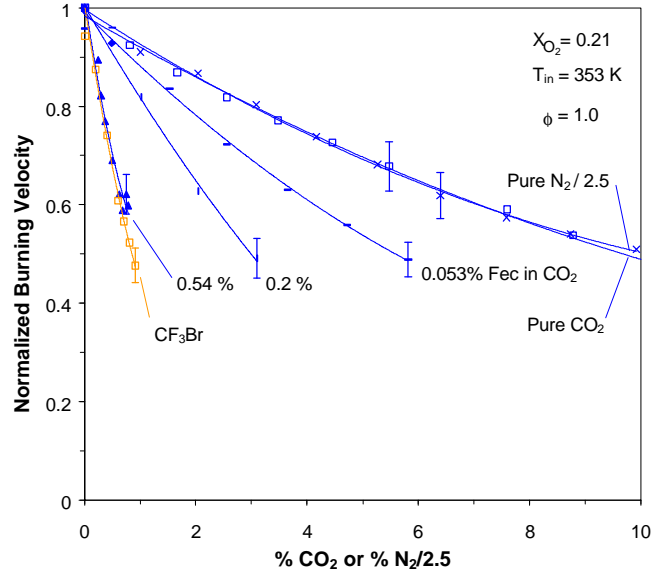

Figure 2 - Normalized burning velocity of CH$_4$/O$_2$/N$_2$ flames inhibited by pure CO$_2$ and pure N$_2$, and by blends of CO$_2$ and ferrocene. The equivalent percentage of ferrocene in CO$_2$ is given, and data for CF$_3$Br are shown for comparison.
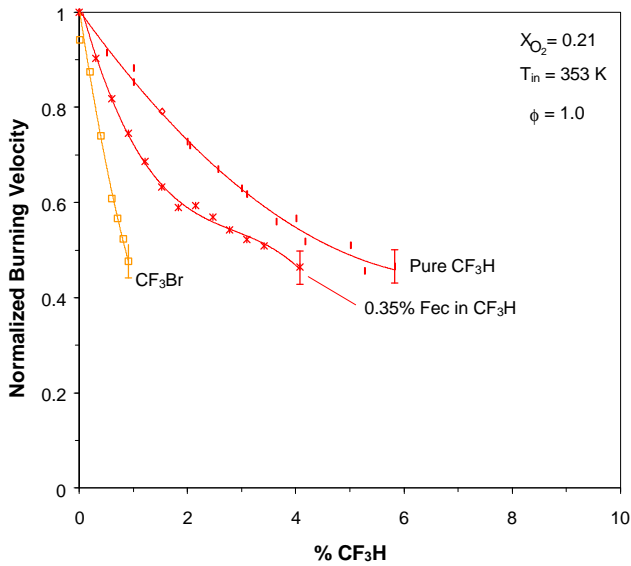

Figure 3 - Normalized burning velocity of premixed CH$_4$/O$_2$/N$_2$ flames inhibited by pure CF$_3$H and by CF$_3$H with 0.35% ferrocene, together with data for CF$_3$Br.
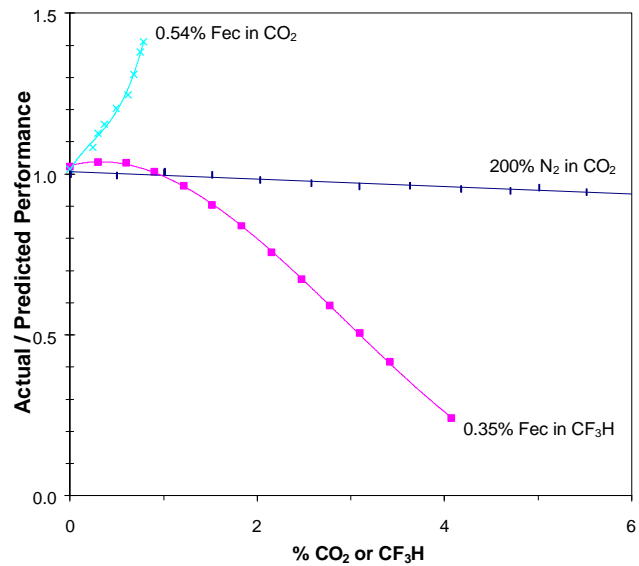

Figure 4 – Index of actual performance of inhibitor blend as compared to the predicted performance based on a linear sum of the burning velocity reduction caused by each component.