

## EXPERIMENTAL STUDY OF THE INHIBITION OF PREMIXED AND DIFFUSION FLAMES BY IRON PENTACARBONYL

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The recent ban on the production of  $\text{CF}_3\text{Br}$  has motivated a search for alternate agents for fire suppression; however, a replacement agent with all of the desirable properties of  $\text{CF}_3\text{Br}$  is proving difficult to find. While most of the research has concentrated on other halogenated agents, there exist agents that are much more effective than  $\text{CF}_3\text{Br}$  but about whose inhibition mechanism less is known. These agents typically involve a condensed phase. This paper investigates the behavior of iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ), one of the most efficient inhibitors identified in the past, in methane/oxygen/nitrogen flames; measurements are reported for both diffusion and premixed flames. The reduction in the extinction strain rate and laminar burning velocity with addition of iron pentacarbonyl is determined over moderate ranges of fuel-air equivalence ratio  $\phi$  and oxygen mole fraction  $X_{\text{O}_2}$ . The flame and inhibitor locations in the counterflow diffusion flame experiments are varied to control the condensed- and gas-phase species transport rates to the flames and the chemical environment for their reaction.

In the premixed flames, iron pentacarbonyl at low concentration reduces the burning velocity up to 100 times more effectively than  $\text{CF}_3\text{Br}$  and shows a strong dependence on both  $\phi$  and  $X_{\text{O}_2}$ ; however, at  $\text{Fe}(\text{CO})_5$  mole fractions above a few hundred ppm, there is no additional reduction of the burning velocity. In diffusion flames,  $\text{Fe}(\text{CO})_5$  is again shown to be more effective at the lowest concentrations, but the inhibition effect does not level off at higher mole fractions as it does in the premixed flames. In addition, combinations of flame and inhibitor location in the counterflow flames have been found for which iron pentacarbonyl either provides negligible inhibition at any mole fraction or promotes the combustion. The possible mechanisms are discussed.

### Introduction

The ban on the production of the fire-suppressant  $\text{CF}_3\text{Br}$  has created a need for replacement agents. Obvious alternatives are other halogenated hydrocarbons, and much research has recently been devoted to understanding their relative performance and inhibition mechanisms [1-3]. However, an agent with all of the desirable properties of  $\text{CF}_3\text{Br}$  is proving difficult to find. Consequently, additional research is necessary to identify new suppressants and understand the mechanisms of inhibition of known, effective agents.

Metal compounds have been found to be up to several orders of magnitude more effective flame suppressants than the halogens [4]. In particular, iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , was found to be one of the strongest inhibitors—up to two orders of magnitude more effective than  $\text{CF}_3\text{Br}$  at reducing the burning velocity of premixed hydrocarbon-air flames [5,6]. While research has been conducted to understand metals in hydrocarbon flames and progress has been made, a thorough description of the mechanisms of inhibition provided by these agents has yet to be delineated.

Iron pentacarbonyl forms condensed-phase par-

ticulates upon passing through a flame. Interestingly, other very effective inhibitors also involve a condensed phase. These inhibitors include those that form the particulates after passing through the flame as well as those that are initially added as a condensed phase. The former category includes other organometallic compounds such as lead tetraethyl and nickel carbonyl and the halometallic compounds  $\text{TiCl}_4$  and  $\text{SnCl}_4$  [4], as well as a new class of fire suppressants, pyrotechnically generated aerosols [7], which may work similarly. The latter category includes the widely used alkali salt powders  $\text{NaHCO}_3$  and  $\text{KHCO}_3$  [8], other metal salts [9], and a new type of suppressant, nonvolatile organic precursors [10]. These condensed-phase agents have many similarities, in particular, their strong inhibiting action and the lack of a complete understanding of their modes of inhibition. Because  $\text{Fe}(\text{CO})_5$  is so effective, it was selected first for further study. Although its toxicity prevents it from being used as a flame suppressant, an understanding of its inhibition mechanism may be helpful for developing new agents, and the experimental and analytical tools being developed will be useful for the study of other heterogeneous inhibitors.

The present approach is to use simple laboratory

flames, both premixed Bunsen type and counterflow diffusion, to obtain fundamental information on the action of iron pentacarbonyl. The burning velocity and extinction strain rate, both of which provide a measure of the overall reaction rate, are determined with addition of  $\text{Fe}(\text{CO})_5$ , while varying the stoichiometry, oxygen mole fraction, flame temperature, and flame location. These experiments allow control of the chemical environment, the location where the metal-containing species are formed, and the transport of these species to the reaction zone.

### Background

In comprehensive studies of the influence of numerous additives on the flammability limits and burning velocity of carbon monoxide and hydrocarbon flames, Lask and Wagner [4] found iron pentacarbonyl to be a powerful flame inhibitor. Other screening experiments confirmed these findings, including the premixed hydrogen-air tests by Miller et al. [11], the low-pressure, spherical diffusion flame and premixed flame experiments by Miller [12], and the partially premixed ethanol pool-burner investigations of Vanpee et al. [9].

The most detailed studies of iron pentacarbonyl inhibition are the studies of Wagner and co-workers [5,6]. They found that the inhibition by  $\text{Fe}(\text{CO})_5$  decreases at pressures below atmospheric and that iron pentacarbonyl is more effective in  $\text{CH}_4$ -air than in  $\text{CH}_4$ - $\text{O}_2$  flames. For low  $\text{Fe}(\text{CO})_5$  concentrations, the reduction in the burning velocity is proportional to the inhibitor concentration, whereas for higher concentrations the relative influence of  $\text{Fe}(\text{CO})_5$  seems to decrease [5]. In flame structure measurements with low-pressure, premixed methane/oxygen/nitrogen flames [6], iron pentacarbonyl increases the rate of OH recombination downstream of the reaction zone. Unfortunately, in the low-pressure flames where a detailed investigation of the reaction zone is possible and the measurements were made, the effect of  $\text{Fe}(\text{CO})_5$  is small. Although the results were not final, the authors proposed that the inhibition may be through homogeneous reactions at low inhibitor concentrations and heterogeneous reactions at high inhibitor concentrations [6]. Other flame experiments incorporating  $\text{Fe}(\text{CO})_5$  include studies on antiknock agents [13,14], soot [15-17], and flame synthesis of particles [18], but no conclusion can be drawn easily from those concerning the mechanism for flame inhibition.

The strong inhibiting action of  $\text{Fe}(\text{CO})_5$  is not explained by any of the preceding studies, many of which screen a large number of compounds rather than investigating one compound in detail. In addition, diffusion flames, which are more representative of fires than premixed flames, have not been used for any systematic study of the inhibition effect of

$\text{Fe}(\text{CO})_5$ . To overcome these shortcomings, the present paper investigates the addition of iron pentacarbonyl to laboratory flames of both premixed and diffusion type and presents fundamental data that can be used for future comparison with modeling results.

### Premixed Flames

#### Experimental

The decrease in the laminar burning velocity of a premixed flame (1.02-cm-diameter nozzle burner, 1.3-cm-tall Bunsen flame) is used in the present work as a measure of the inhibition action of iron pentacarbonyl. The experimental system has been described in detail previously [19,20]. The fuel gas is methane, and the oxidizer stream consists of nitrogen and oxygen. Part of the nitrogen stream is diverted and bubbles through liquid  $\text{Fe}(\text{CO})_5$  in a two-stage saturator in an ice bath. This carrier flow (always less than 0.4 l/min) is assumed to be saturated. The inhibitor concentration in the premixed gases is increased, and the total flow is reduced as necessary to obtain the desired flame height while maintaining constant values of the stoichiometry and the oxygen and  $\text{Fe}(\text{CO})_5$  mole fractions. The average burning velocity for the flame is determined using the total area method assuming a constant value for the flame area. Individual flows are measured with an accuracy of  $\pm 1\%$ , and the largest uncertainty in the measurement of the average burning velocity is the schlieren image area (which was not measured in the present work). Since the burner produces schlieren and visible images that are very nearly straight-sided and parallel, the flame area has been found to remain within a few percentages if the flame height is fixed (even as the burning velocity is reduced by 60%). Consequently, the average burning velocities as measured for the present burner are believed to be accurate to within about 5%. Because the relative change in the burning velocity can be measured with more confidence than its absolute value, the burning velocity reduction is normalized by the uninhibited burning velocity.

#### Results and Discussion

The uninhibited premixed flame is blue. Addition of 10 ppm of  $\text{Fe}(\text{CO})_5$  turns the flame orange, and the intensity increases with increasing  $\text{Fe}(\text{CO})_5$  mole fraction. The orange emission is uniformly bright in the postcombustion region for about 1 cm downstream, and the intensity appears greatest in the reaction zone of the flame.

The normalized burning velocity of the premixed methane-air flame inhibited by iron pentacarbonyl is shown in Fig. 1a for a fuel/air equivalence ratio  $\phi$

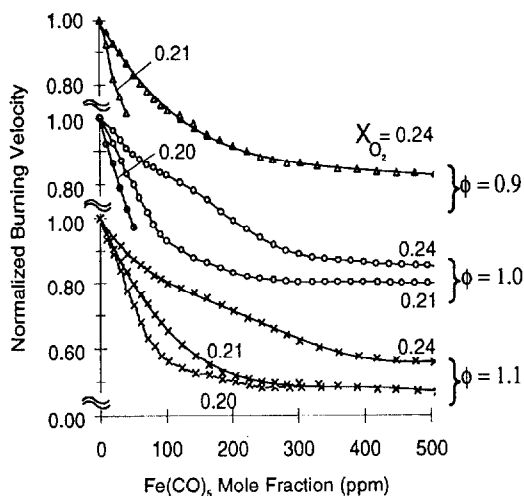
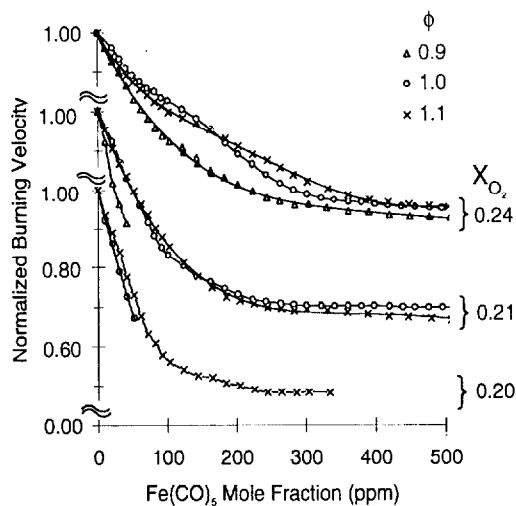


FIG. 1. Normalized burning velocity of premixed  $\text{CH}_4/\text{O}_2/\text{N}_2$  flames with  $X_{\text{O}_2} = 0.20, 0.21,$  and  $0.24$  and  $\phi = 0.9, 1.0,$  and  $1.1$ ; (a) grouped by  $X_{\text{O}_2}$  and (b) grouped by  $\phi$ .

of 0.9, 1.0, and 1.1, and three values of the oxygen mole fraction  $X_{\text{O}_2} = 0.20, 0.21,$  and  $0.24$  (except the case of  $X_{\text{O}_2} = 0.20$  and  $\phi = 0.9$  where a flame could not be stabilized). For  $X_{\text{O}_2} = 0.21$ , the stoichiometric and rich flames are affected about equally by the  $\text{Fe}(\text{CO})_5$ , while the lean flame shows twice as much reduction in the burning velocity at low  $\text{Fe}(\text{CO})_5$  concentrations and could not be stabilized above 41 ppm, where the burning velocity reduction is 30%. Most notably, above about 200 ppm in the stoichiometric and rich flames with  $X_{\text{O}_2} = 0.21$ , there does not appear to be any additional inhibition effect. At all values of  $X_{\text{O}_2}$ , the rich and stoichiometric flames

TABLE 1  
Calculated final temperature  $T$ , H-radical superequilibrium, and burning velocity  $V_{\text{cal}}$ , as well as measured burning velocity  $V_{\text{exp}}$  and inhibition index  $\Phi_0$  at zero inhibitor mole fraction. Data are presented for the experimental conditions of Fig. 1.

| $\phi$ | $X_{\text{O}_2}$ | $T$  | $\frac{[\text{H}]_{\text{peak}}}{[\text{H}]_{\text{eq.}}}$ | $V_{\text{cal}}$ | $V_{\text{exp}}$ | $\Phi_0$ |
|--------|------------------|------|--|------------------|------------------|----------|
| 0.9    | 0.21             | 2131 | 41.9   | 36.7             | 37.1             | 1648     |
| 0.9    | 0.24             | 2285 | 15.3   | 52.7             | 51.4             | 781      |
| 1.0    | 0.20             | 2175 | 22.1   | 35.8             | 33.2             | 1400     |
| 1.0    | 0.21             | 2232 | 16.5   | 41.8             | 40.6             | 850      |
| 1.0    | 0.24             | 2358 | 8.6  | 57.4             | 59.2             | 479      |
| 1.1    | 0.20             | 2152 | 15.2   | 36.5             | 33.8             | 1086     |
| 1.1    | 0.21             | 2213 | 11.7   | 41.8             | 39.3             | 845      |
| 1.1    | 0.24             | 2363 | 6.5  | 57.5             | 53.4             | 647      |

behave similarly, while the lean flames are inhibited more.

To more clearly show the effect of oxygen mole fraction, the data in Fig. 1a are replotted in Fig. 1b, grouped by  $\phi$ . As the figure indicates, there is a strong effect of oxygen mole fraction on the initial inhibitory effect, with  $\text{Fe}(\text{CO})_5$  decreasing the burning velocity a factor of about 3.5 less effectively at an oxygen mole fraction of 0.24 as compared to 0.20. At low oxygen mole fractions ( $X_{\text{O}_2} = 0.20$  and  $0.21$ ), the burning velocity drops rapidly up to an  $\text{Fe}(\text{CO})_5$  mole fraction of around 100 ppm and then approaches a constant value for all higher  $\text{Fe}(\text{CO})_5$  loadings. Conversely, at higher oxygen mole fraction ( $X_{\text{O}_2} = 0.24$ ), the decrease in burning velocity is more gradual but continues to higher  $\text{Fe}(\text{CO})_5$  loadings, 300–500 ppm for these conditions. The final inhibited burning velocity is somewhat higher as the oxygen mole fraction increases.

To allow a comparison of the variations in the inhibitor's effectiveness with flame properties, numerical calculations were performed for the uninhibited flames. Note that addition of these small amounts of iron pentacarbonyl has very little effect on the thermodynamic properties of these near-stoichiometric methane-air flames, with the adiabatic flame temperature changing by less than 6 K for 500 ppm of  $\text{Fe}(\text{CO})_5$  reacting to  $\text{FeO}$ . The flame structure is obtained using the Sandia PREMIX [21] flame code with GRI-Mech version 1.2 [22] for premixed, freely propagating flames at the conditions of the experiments. Table 1 lists the equivalence ratio and oxygen mole fractions for the uninhibited flames presented in Fig. 1, as well as the calculated adiabatic flame temperature, superequilibrium for H radical, and burning velocity. Also listed in the table are the experimentally measured burning velocities of the uninhibited flames and the slope of the inhibitory effect

at zero iron pentacarbonyl mole fraction, expressed as the inhibition index suggested by Fristrom and Sawyer [23],  $\Phi_0 = -dV_i/dX_i X_{O_2}/V_i$ , where  $V_i$  and  $dV_i/dX_i$  are the burning velocity and slope of the burning velocity reduction with inhibitor addition at zero inhibitor and  $X_{O_2}$  is the oxygen mole fraction. The inhibition index  $\Phi_0$  for iron pentacarbonyl is seen to range from about 500 to 1600; as Fig. 1 shows, the index goes to zero above 300–500 ppm. The value of  $\Phi_0$  for  $CF_3Br$ , which shows little variation with  $CF_3Br$  mole fraction, is only about 20 [24], indicating the superior effectiveness of  $Fe(CO)_5$ .

Many researchers have collected evidence that metals and metal oxides at ppm concentrations catalyze H and OH recombination and have proposed gas-phase catalytic cycles involving metal hydroxide intermediates [8,25–28]. Others [13,14,28,29] provide evidence for a heterogeneous effect. Kaufman [30] has observed catalysis of O-atom recombination on surfaces coated with  $Fe(CO)_5$  decomposition products. Since premixed flames typically have peak O-, H-, and OH-radical concentrations in excess of equilibrium values, it is possible that the variation in iron pentacarbonyl's effectiveness in these flames is related to the degree of superequilibrium. As Table 1 shows, the leaner, lower-temperature flames have higher H-atom superequilibrium, and these flames also have the largest values of  $\Phi_0$ . The magnitude of the superequilibrium is about the same for OH and an order of magnitude less for O; however, OH and O superequilibrium are uncorrelated with  $\Phi_0$  for iron pentacarbonyl. These results are consistent with an inhibition mechanism involving catalytic recombination of H atoms by an iron compound.

The variation in iron pentacarbonyl's inhibitory effect with oxygen mole fraction, as well as the decrease in its effectiveness with increasing iron pentacarbonyl mole fraction, has been quantified. These data supplement the findings of Wagner et al. [4–6]. The next section describes the behavior of iron pentacarbonyl in counterflow diffusion flames, which have a different structure than premixed flames.

### Counterflow Diffusion Flames

#### Experimental

The burner used for the counterflow experiments is described in Ref. 31, and the experimental setup and procedure are described in detail in Ref. 20. The fuel gas is methane; the oxidizer gas is produced by mixing nitrogen and oxygen. The iron pentacarbonyl is added to the fuel or the oxidizer stream by bubbling methane or nitrogen through a two-stage saturator in a water bath at a controlled temperature of 17–22°C. The gas flow lines that are located after the saturator but before the point of dilution by the

bulk of the gas flow are maintained at 39°C to prevent condensation of the  $Fe(CO)_5$ . All experiments are performed at ambient pressure and with the gas flows at ambient temperature.

The reduction in the extinction strain rate is used as a measure of the inhibition action of iron pentacarbonyl. The strain rate, seen as the maximum value of the oxidizer-side velocity gradient before the flame, can be approximated [32] from the outer flow jet exit velocities according to

$$a_0 = \frac{2|v_0|}{L} \left( 1 + \frac{|v_F| \sqrt{\rho_F}}{|v_0| \sqrt{\rho_0}} \right)$$

Here,  $L$  denotes the distance between the ducts,  $v$  the velocity,  $\rho$  the density, and the subscripts  $F$  and  $0$  the fuel and oxidizer stream. The jet exit velocities are chosen so that the momentum of the two streams is balanced at all values of the strain rate; that is,  $\rho_F v_F^2 = \rho_0 v_0^2$ . That choice ensures that the flame, which is usually close to the stagnation plane, is kept approximately equidistant from the two ducts. If the flame sits on the fuel side of the stagnation plane, the strain rate (i.e., velocity gradient) on the fuel side is calculated by

$$a_F = \sqrt{\frac{\rho_0}{\rho_F}} a_0$$

When the critical value of the strain rate is reached, the flame extinguishes abruptly; this value is recorded as the extinction strain rate that is found with an uncertainty of  $\pm 5\%$ .

To support the experiments, numerical calculations are performed for uninhibited gas-phase counterflow diffusion flames (at present, the condensed phase and iron reactions are not included). The numerical code of Smooke [33] is used with a one-carbon mechanism for methane oxidation [34].

#### Results and Discussion

The flame can be positioned on either the fuel or the oxidizer side of the stagnation plane, depending on the dilution of the fuel and the oxidizer stream. Additionally, the inhibitor can be added to either the fuel or the oxidizer stream, thereby influencing the possible reactions and the transport of the inhibitor to the reaction zone [35]. Results for each case are discussed later in this section.

Figure 2 shows the extinction strain rate versus the molar concentration (in ppm) of inhibitor for all cases of flame location and inhibitor injection mentioned previously. For the case of undiluted air versus undiluted methane (where the flame is located on the oxidizer side of the stagnation plane), the addition of iron pentacarbonyl to the oxidizer stream decreases the extinction strain rate rapidly for mole fractions up to 80 ppm (filled squares). Above this value, the extinction strain rate decreases less rapidly

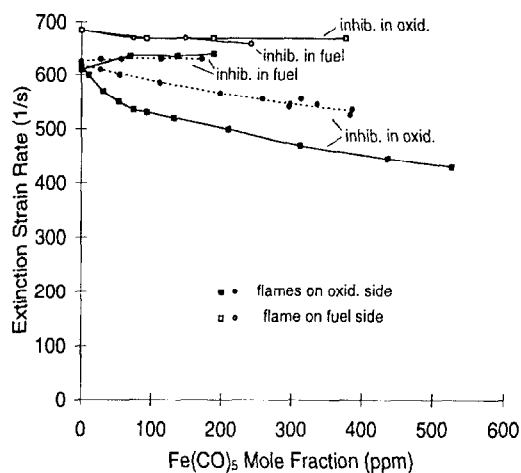


FIG. 2. Extinction strain rate versus  $\text{Fe}(\text{CO})_5$  mole fraction for counterflow diffusion flames.  $\text{Fe}(\text{CO})_5$  is added to either the fuel or oxidizer stream for each case. Reactant stream mole fractions are (1) undiluted air versus undiluted methane-filled squares (flame on oxidizer side), (2) 45%  $\text{O}_2/55\% \text{N}_2$  versus 13%  $\text{CH}_4/87\% \text{N}_2$ -open symbols (flame on fuel side), (3) 30%  $\text{O}_2/70\% \text{N}_2$  versus 20%  $\text{CH}_4/80\% \text{N}_2$ -filled circles (flame on oxidizer side).

but roughly in proportion to the increase in  $\text{Fe}(\text{CO})_5$ . Nevertheless, up to the amount of inhibitor used in the experiment (which was limited by the saturator), the incremental inhibiting effect of  $\text{Fe}(\text{CO})_5$  does not become zero as in the premixed flame. The inhibition effect of  $\text{Fe}(\text{CO})_5$  added to the air stream of a counterflow diffusion flame is much stronger than that of  $\text{CF}_3\text{Br}$ : an  $\text{Fe}(\text{CO})_5$  mole fraction of 500 ppm reduces the extinction strain rate by about 30%, whereas 5000 ppm of  $\text{CF}_3\text{Br}$  are necessary for a reduction of about 20% [36,37]. When the iron pentacarbonyl is added to the oxidizer, the originally blue flame changes to very luminous, bright orange, likely because of the formation of  $\text{FeO}$ , which has strong emission at 591 nm [6]. A deposition of red/orange particles, presumably iron oxides, is observed in the exhaust system after the experiments.

Contrary to the strong inhibition effect discussed previously, adding  $\text{Fe}(\text{CO})_5$  to the fuel stream of the same flame increases the extinction strain rate (filled squares). This increase is small compared to the magnitude of the decrease from addition to the oxidizer stream but is noticeable and repeatable. This flame does not change its color but remains blue.

Contrasting results were obtained for a flame on the fuel side of the stagnation plane, which was achieved with an oxidizer stream of 45%  $\text{O}_2/55\% \text{N}_2$  (all values are given as molar concentrations) and a fuel stream of 13%  $\text{CH}_4/87\% \text{N}_2$  (open symbols). Figure 2 shows the effect of adding  $\text{Fe}(\text{CO})_5$  to

oxidizer and fuel stream, respectively. In both cases, the strain rate at extinction decreases slightly, a few percentage points at an inhibitor mole fraction of 80 ppm, above which there is no additional effect. Overall, the inhibiting effect of adding iron pentacarbonyl to this flame is almost negligible. For the addition of  $\text{Fe}(\text{CO})_5$  to the fuel or the oxidizer stream, a red layer formed on the side of the blue flame facing the iron pentacarbonyl injection.

The flame on the fuel side, for the conditions reported, is cooler and located closer to the stagnation plane than the flame on the oxidizer side for undiluted air and methane. To reduce these differences, the condition of 30%  $\text{O}_2/70\% \text{N}_2$  versus 20%  $\text{CH}_4/80\% \text{N}_2$  was chosen for a subsequent experiment. According to the calculations, this condition gives a flame on the oxidizer side that is more comparable to the flame on the fuel side with respect to maximum temperature and location of this maximum in relation to the stagnation plane.

Figure 2 shows the experimental results of adding  $\text{Fe}(\text{CO})_5$  to this flame of 30%  $\text{O}_2/70\% \text{N}_2$  versus 20%  $\text{CH}_4/80\% \text{N}_2$  (filled circles). As seen before, adding iron pentacarbonyl to the oxidizer stream decreases the extinction strain rate and adding it to the fuel stream increases the extinction strain rate. Neither effect is as pronounced as in the case of higher flame temperature (filled squares), but the same qualitative behavior is observed. The inhibiting action does not level off at 400 ppm, and the effect is slightly greater for mole fractions less than 100 ppm. Since the major difference between the flame on the fuel side (open symbols) and the cooler flame on the oxidizer side (filled circles) is the flame location relative to the stagnation plane, it appears that not only the temperature but also the transport rates and the chemical environment influence the action of iron pentacarbonyl in these flames.

To study the effect of the oxygen mole fraction, its value was changed for the case of a flame on the oxidizer side and adding the inhibitor to the oxidizer stream, while keeping the stoichiometric mixture fraction constant. The stoichiometric mixture fraction [38] is

$$Z_{st} = \left( 1 + \frac{\nu_{\text{O}_2} M_{\text{O}_2} Y_{\text{CH}_4,F}}{\nu_{\text{CH}_4} M_{\text{CH}_4} Y_{\text{O}_2,O}} \right)^{-1}$$

where  $\nu_i$  denotes the stoichiometric coefficient of species  $i$ ,  $M_i$  the molecular mass,  $Y_i$  the mass fraction, and  $F$  and  $O$  the fuel and oxidizer stream. A constant value of 0.0622 was used for  $Z_{st}$ .

Figure 3 shows the normalized extinction strain rate ( $a_{\text{ext}}/a_{\text{ext},0\% \text{inhibitor}}$ ) versus the molar concentration of iron pentacarbonyl for three different values of the oxygen mole fraction  $X_{\text{O}_2}$ . The inhibiting effect for  $X_{\text{O}_2} = 0.21$  and  $X_{\text{O}_2} = 0.215$  is almost the same, whereas the inhibiting effect is stronger for  $X_{\text{O}_2} = 0.205$ . The results suggest that, as in the

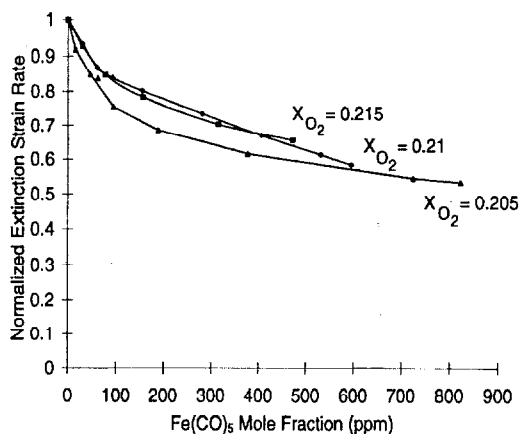


FIG. 3. Normalized extinction strain rate versus  $\text{Fe}(\text{CO})_5$  mole fraction for counterflow diffusion flames at three values of  $X_{\text{O}_2}$  and a constant stoichiometric mixture fraction  $Z_{st} = 0.0622$  (flame on oxidizer side, inhibitor in oxidizer stream).

premixed flame described previously, the oxygen mole fraction has a strong influence on the effectiveness of iron pentacarbonyl in the counterflow diffusion flame. To confirm these results, more experiments will be run with a broader range of values for  $X_{\text{O}_2}$ . (Since counterflow diffusion flames are very sensitive to the oxygen content of the oxidizer stream, even uninhibited flames have low extinction strain rates at low values of  $X_{\text{O}_2}$ , thereby limiting the practicable range of  $X_{\text{O}_2}$ .)

The reasons for the inhibiting and promoting behavior of  $\text{Fe}(\text{CO})_5$  in the counterflow flames described are still unclear. The present data showing inhibition are consistent with both the homogeneous and heterogeneous mechanisms of catalytic recombination of radicals. As mentioned before, many researchers found indications that metals and metal oxides catalyze H- and OH-radical recombination via metal hydroxide intermediates [8,25–28]. With the flame on the oxidizer side and  $\text{Fe}(\text{CO})_5$  in the oxidizer stream, all of the agent reaches the reaction zone and oxygen is available for forming oxygenated iron intermediates, which is in support of this mechanism.

The increase in the extinction strain rate when iron pentacarbonyl is added to the fuel stream with the flame on the air side is in accord with the gas-phase mechanism of Cotton et al. [39]. They proposed that when subequilibrium radical concentrations exist, the catalytic reaction cycle mentioned previously can run in the reverse direction to increase radical concentrations. The numerical simulations for the uninhibited flames indicate that subequilibrium radical concentrations exist at some locations on the fuel side of the stagnation plane,

whereas superequilibrium concentrations prevail at the oxidizer side of the flame. These observations support the proposed mechanism.

Since the condensed-phase species are probably iron oxides, and oxygen is needed for their formation, most of the preceding observations are also consistent with a heterogeneous catalytic mechanism. Finally, the reduced effect of iron pentacarbonyl at higher concentrations in the diffusion and premixed flame can be rationalized with either homogeneous or heterogeneous mechanisms. Above a certain iron mole fraction in the flame, the gas-phase catalytic iron intermediate may no longer be the deficient reactant. Conversely, if it is a surface effect, above a certain iron loading in the flame, the particles may agglomerate faster than new particles are formed, which results in no increase in the total surface area for inhibition.

The present experimental results elucidate many details of the inhibition by  $\text{Fe}(\text{CO})_5$ , but they do not reveal its precise mechanism. Particle measurements are planned to learn more about the homogeneous or heterogeneous reaction mechanism.

### Summary

The inhibiting action of iron pentacarbonyl on the burning velocity and extinction strain rate of premixed and diffusion flames of methane, oxygen, and nitrogen has been examined systematically. In premixed flames, behavior at low and high iron pentacarbonyl mole fractions is distinctly different: the reduction in burning velocity is very strong for an inhibitor mole fraction up to about 100 ppm, above which there is negligible additional inhibition. In the lower range of iron pentacarbonyl concentrations, richer flames or higher oxygen mole fraction reduce the inhibitory effect, while at iron pentacarbonyl mole fractions near 500 ppm, the burning velocity reduction is slightly greater at lower oxygen mole fraction. In counterflow diffusion flames with the flame on the oxidizer side of the stagnation plane and iron pentacarbonyl added to the oxidizer stream, the inhibitory effect is also very strong. The rate of decrease in extinction strain rate is greatest for iron pentacarbonyl mole fractions below 100 ppm; however, in contrast to the premixed flames, the inhibition effect continues even above 500 ppm. The effect of reduced oxygen mole fraction is similar in the premixed and diffusion flames. Interestingly, when  $\text{Fe}(\text{CO})_5$  is added to the fuel stream in the diffusion flame, there is an apparent promotion of the combustion. Finally, when the flame is located on the fuel side, there is a negligible effect of  $\text{Fe}(\text{CO})_5$  when it is added to either stream. These results appear to be consistent with an inhibition mechanism involving catalytic recombination of H radicals; homogeneous or heterogeneous reactions might be

responsible. The data provide an extensive basis for planned additional research, including particle measurements and numerical modeling of the condensed phase.

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## COMMENTS

*E. Metcalfe, University of Greenwich, UK.* Can you compare the effectiveness of inhibition of ferrocene with iron pentacarbonyl? Would it be possible to add a suspension of fine iron oxide particles to the gas flow to test the mechanism?

It is very interesting to note the parallel between your work on flame inhibition, and the studies on ferrocene as flame retardant/smoke suppressant in polymers such as PVC, where a similar mechanism appears to be occurring.

*Author's Reply.* The questioner has raised two excellent points. We are not aware of any systematic studies on the inhibition of laboratory flames by ferrocene, but would expect it to be similar to that of iron pentacarbonyl. In continuing work, we would like to examine the inhibitory effect of other iron compounds including ferrocene and various iron oxides.