

# INHIBITION OF PREMIXED METHANE-AIR FLAMES BY IRON PENTACARBONYL

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**Introduction:** Brominated fire suppressants are effective and widely used [1]. Due to their destruction of stratospheric ozone, however, the production of these chemicals was halted in January 1994. Although testing and development of possible substitutes is occurring [2], a replacement with all of the desirable properties of  $\text{CF}_3\text{Br}$  (the most common fire suppressant) has yet to be identified. Consequently, the Fire Science Division at the National Institute of Standards and Technology (NIST) is conducting research to identify new chemical inhibitors, understand the mechanisms of inhibition of known or widely used agents, and evaluate the performance of proposed agents.

Iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , a highly flammable, viscous liquid (boiling point 103 C; melting point -20 C), has been shown to be two orders of magnitude more effective than  $\text{CF}_3\text{Br}$  [3]. Nonetheless, its mechanism of inhibition in premixed flames has not been clearly discerned, and it has not been tested in diffusion flames, which are more representative of fires. Although one would never use iron pentacarbonyl to extinguish fires because of its high toxicity, it is so efficient that an understanding of its inhibition mechanism may provide possible avenues for developing new inhibitors. Iron pentacarbonyl forms solid particulates ( $\text{Fe}_2\text{O}_3$ ) upon passing through a flame. Other condensed phase agents, such as sodium and potassium bicarbonate, have also been found to be strong flame inhibitors, about 3.5 times as effective as  $\text{CF}_3\text{Br}$  on a mass basis [4]. Despite their widespread use, little is known about their flame inhibition mechanisms. An understanding of inhibition by  $\text{Fe}(\text{CO})_5$  can serve as a basis for interpreting the influence of condensed phase agents on flame chemistry. In addition, a new class of compounds, pyrotechnically generated aerosols [5], may involve similar inhibition mechanisms to those of  $\text{Fe}(\text{CO})_5$  since some of these also generate metals and metal oxides in a flame.

The inhibition of premixed flames by iron pentacarbonyl was studied in the 1960's [3,6]. Recently,  $\text{Fe}(\text{CO})_5$  has been used to study the influence of iron additives on soot formation [7], and the formation of iron-oxide/silica superparamagnetic nanocomposites [8,9]. Attempts were made at understanding its mechanism of inhibition in low pressure, premixed flames [6]. However, due to the rapid adoption of  $\text{CF}_3\text{Br}$ , the studies were discontinued and remain inconclusive, and a detailed description of the inhibition mechanism of  $\text{Fe}(\text{CO})_5$  for premixed flames does not appear in the literature. Although there is some evidence that the mechanism for premixed systems may involve hydrogen atom recombination at the surface of iron oxide particles [10,11], or gas-phase reactions of Fe and FeO [6], the relative roles of thermal effects and heterogeneous and gas phase chemistry remain unclear even for premixed flames. Moreover, most fires are better represented as atmospheric pressure diffusion flames, which have structures very different from premixed flames.

It is of interest to determine if the extraordinary effectiveness of  $\text{Fe}(\text{CO})_5$  in premixed flames also manifests itself in diffusion flames.

The goal of the present study is to investigate the mechanisms of inhibition of iron pentacarbonyl in counterflow diffusion flames of methane and air. However, preliminary experiments with counterflow flames yielded unexpected results: at a strain rate of about  $50 \text{ s}^{-1}$  with streams of pure methane and air, it was not possible to extinguish the flames even at air stream  $\text{Fe}(\text{CO})_5$  mole fractions of 45 times the concentration found to reduce the burning rate of premixed methane-air flames by 25% [3]. For comparison, the fluorinated agent  $\text{CF}_3\text{H}$  extinguishes a similar methane-air counterflow diffusion flame at a concentration in the air stream of only about seven times that which reduces the burning rate of premixed flames by 25%. Consequently, it was decided to first conduct premixed flame tests, and this abstract presents some interesting new results from these experiments.

### Experiment

The laminar burning velocity is used in the present work as a measure of the inhibition action of the iron pentacarbonyl. A Mache-Hebra [12] nozzle burner 1.02 cm in diameter produces a 1.3 cm tall Bunsen flame. The experimental system has been described previously [13]. In the present work, however, the flame height is held constant and no schlieren images are taken of the flame. Since the burner produces schlieren and visible images which are very nearly straight-sided and parallel, the flame area has been found to remain nearly constant if the flame height is held constant. For these experiments, the inhibitor concentration in the premixed gases is increased and the total flow rate reduced as necessary to maintain the desired flame height. The average burning rate for the flame is determined using the total area method. Although measurement of a true one-dimensional, planar, adiabatic burning rate is difficult [14], the relative change in the burning rate can be measured with more confidence. Consequently, the burning rate reduction in the present work is normalized by the uninhibited burning rate.

The burner is placed in a square acrylic chimney with no co-flowing gases. Fuel, air, and carrier gas flows are measured with digitally-controlled mass flow controllers (Sierra Model 860<sup>\*\*</sup>) with a claimed precision of 0.2 % and accuracy of 1 %, which have been calibrated with bubble and dry (American Meter Co. DTM-200A) flow meters so that their accuracy is  $\pm 1\%$ . The fuel gas is methane (Matheson UHP) and the  $\text{Fe}(\text{CO})_5$  carrier gas is argon (Airgas). House compressed air (filtered and dried) is used after it has been additionally cleaned by passing it through an  $0.01 \mu\text{m}$  filter, a carbon filter, and a desiccant bed to remove small aerosols, organic vapors, and water vapor. The  $\text{Fe}(\text{CO})_5$  (Aldrich) is added to the argon flow by a two-stage saturator in an ice bath.

### Results

The burning rates of the premixed methane- and propane-air flames inhibited by  $\text{Fe}(\text{CO})_5$  are presented in Figs. 1 and 2. In these figures, the iron pentacarbonyl mole fraction in the argon carrier gas is 0.0104, so the  $\text{Fe}(\text{CO})_5$  mole fraction is about  $10^2$  times the argon mole fraction listed in the figures. Experiments were conducted at values of fuel-air equivalence ratios  $\phi$  equal to 0.9, 1.0 and 1.1. The burning rate is normalized by the uninhibited burning rate at the same stoichiometry. Figure 1 also presents the normalized burning rates for inhibition by argon alone,

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<sup>\*\*</sup> Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental 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.

and shows the data of Lask and Wagner [3] for comparison. At inhibitor concentrations less than about 80 ppm, the effect of stoichiometry, even over the narrow range of  $\phi$  equal to 0.9 to 1.0, is significant: the lean and rich flames are inhibited 30 and 60% less than the stoichiometric flames. The present data show a 20% reduction in burning rate with an  $\text{Fe}(\text{CO})_5$  mole fraction of only 24 ppm, while Lask and Wagner required 64 ppm to achieve this reduction. Although the curves for  $\text{Fe}(\text{CO})_5$  also include inhibition caused by the argon carrier gas, Figure 1 indicates that at low concentrations this only accounts for about 4% of the inhibition caused by the  $\text{Fe}(\text{CO})_5$  in carries. Most significant is the finding that at  $\text{Fe}(\text{CO})_5$  concentrations above about 100 ppm, there is virtually no effect of additional iron pentacarbonyl; all of the inhibition is caused by the argon carrier gas. It should be noted that during the experiments the flame luminosity steadily increased as the  $\text{Fe}(\text{CO})_5$  concentration was increased. The likely cause of the increase is  $\text{FeO}$  emission at 591.9 nm [6]. As shown in Fig. 2, the results for propane are similar: there is a mild effect of stoichiometry, and above about 120 ppm, additional  $\text{Fe}(\text{CO})_5$  has no effect on the burning rate. Propane flames are inhibited less by  $\text{Fe}(\text{CO})_5$ . It is interesting to note that for both fuels, the lean flames could not be stabilized at higher iron pentacarbonyl concentrations, whereas the rich flames resisted blow-off at the highest concentrations.

In continuing research, the thermal and chemical influence of  $\text{Fe}(\text{CO})_5$  on premixed and diffusion flames will be modeled in order to interpret these experimental results.

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#### References

1. Gann, R.G. (Ed.), *Halogenated Fire Suppressants*, ACS Symposium Series No. 16, The American Chemical Society, 1975.
2. Grosshandler, W.L., Gann, R.G., and Pitts, W.M., Eds. *National Institute of Standards and Technology*, Gaithersburg MD, NIST SP 861, 1994.
3. Lask, G., Wagner, H.G., *Eighth Symposium (International) on Combustion*, Williams and Wilkins Co., Baltimore, 432, 1962.
4. Grummer, J., Miller, L.F., Bruszak, A.E., Dalverny, L.E., *U.S. Bur. of Mines Rep. of Investigations 7782*, 1973.
5. Sheinson, R.S., Eaton, H.G., Zalosh, R.G., Black, B.H., Salmon, G., Smith, W.D., Brown, R., and Burchell, H., *Halon Options Technical Working Conference*, Albuquerque, N.M., 379, 1994.
6. Bonne, U., Jost, W., Wagner, H.G., *Fire Research Abstracts and Reviews*, 4, 6, 1962.
7. Howard, J.B. and Kausch, W.J., Jr., *Progress in Energy and Combustion Science*, 6, 263, 1980.
8. Zachariah, M.R., Aquino, M.I., Shull, R., and Steel, E. "Formation of Super-paramagnetic Nanocomposites from Vapor Phase Condensation in a Flame," to appear in *Nanostructural Materials*.
9. McMillin, B.K., Biswas, P., and Zachariah, M.R. "In Situ Diagnostics of Vapor Phase Growth of Iron Oxide-Silica Nanocomposites, Part I: 2-D Planar Laser-Induced Fluorescence and Mie Imaging," submitted to the *Journal of Aerosol Science*, Dec. 1994.
10. Cheaney, D.E., Davies, D.A., Davis, A., Hoare, D.E., Protheroe, J., and Walsh-VII, A.D., *Seventh Symposium (International) on Combustion*, Butterworths Scientific Publications, London, 183, 1959.
11. Zimpel, C.F. and Graiff-XI, L.B. *Eleventh Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1015, 1967.

12. Mache, H. and Hebra, A., *Sitzungsber. Osterreich. Akad. Wiss., Abt. IIa*, 150, 157, 1941.
13. Linteris, G.T. and Truett, L.F. "Inhibition of Premixed Methane-Air Flames by Fluoromethanes," submitted to *Combustion and Flame*, Oct. 1994.
14. Andrews, G.E. and Bradley, D., *Combust. Flame*, **18**, 133, 1972.

### Premixed Methane-Air Flame

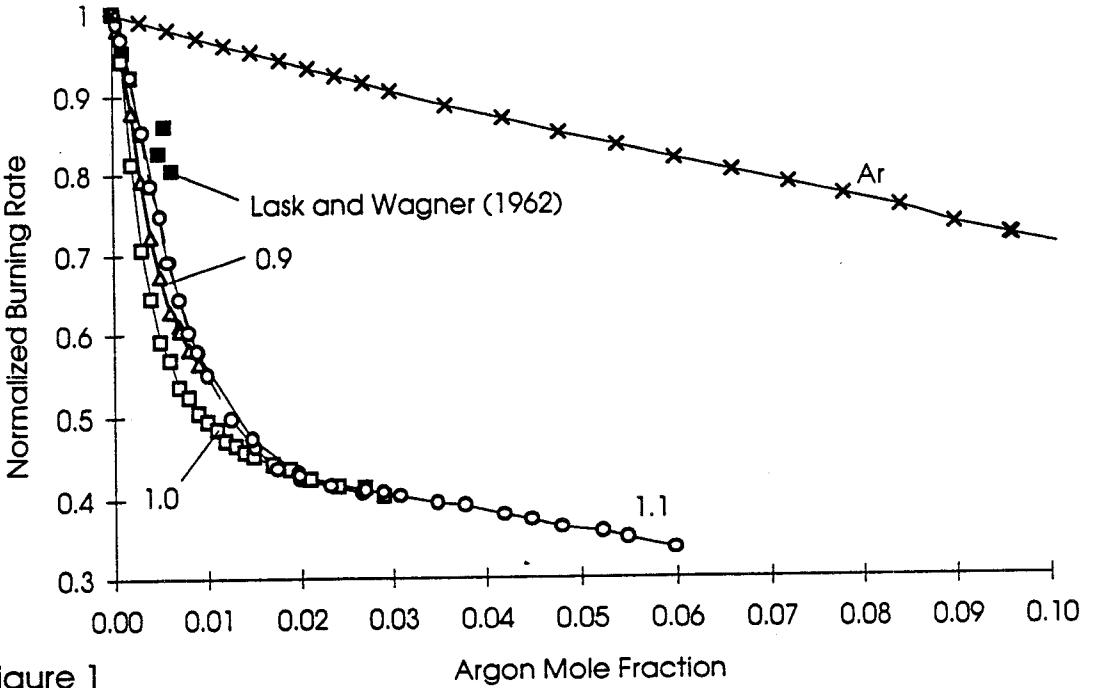


Figure 1

### Premixed Propane - Air Flame

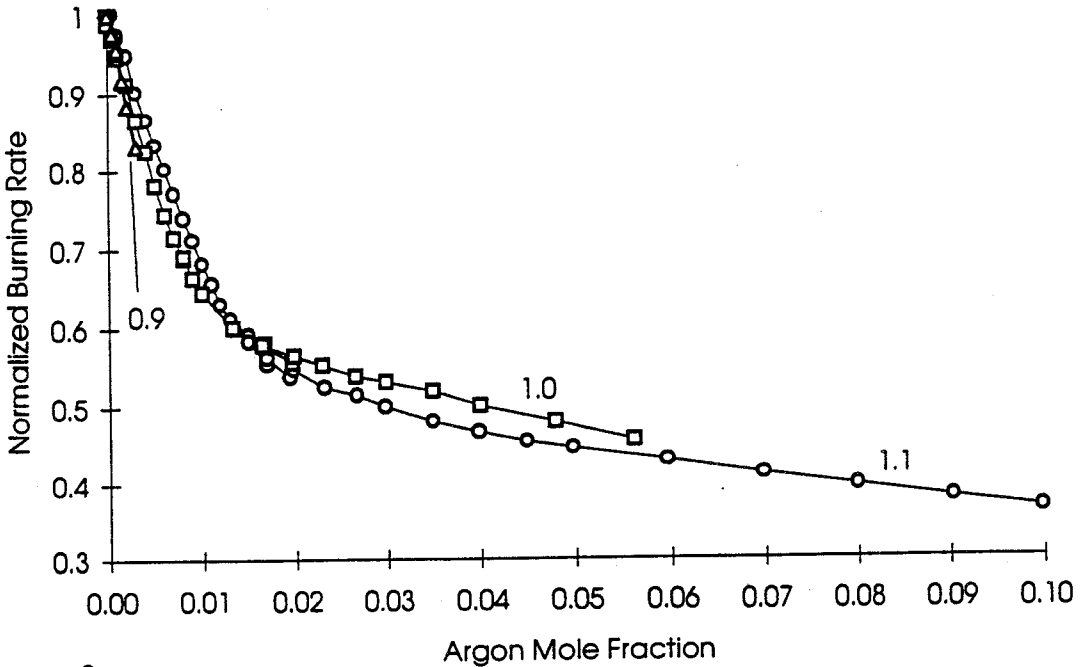


Figure 2

Figures 1 and 2- Normalized burning rate of methane- (Fig. 1) and propane-air (Fig. 2) flames as a function of argon/ $\text{Fe}(\text{CO})_5$  mole fraction for equivalence ratios of 0.9, 1.0, and 1.1. The  $\text{Fe}(\text{CO})_5$  mole fraction is about 1/100 times the argon mole fraction. Figure 1 also shows the burning rate reduction caused by argon alone, as well as the data of Lask and Wagner [3].