THE ROLE OF THE ·CF_3 RADICAL IN EXTINGUISHMENT

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INTRODUCTION

Among the reactions that can be written for the ·CF_3 radical are the following.

$$HCF_3 + \cdot H \rightarrow H_2 + \cdot CF_3 \quad (1)$$

$$\cdot CF_3 + \cdot H \rightarrow HCF_3 \quad (2)$$

$$HCF_3 + \cdot OH \rightarrow H_2O + \cdot CF_3 \quad (3)$$

Taken as a group, these three reactions suggest that the ·CF_3 radical might be involved in one or more catalytic cycles that remove flame propagating radicals from the flame. Reaction (1) is, of course, the primary elementary reaction by which HCF_3 is introduced into the chemistry of the flame, and occurs readily in typical flames. By contrast with HCF_3, CF_4 is relatively unreactive in flames; the abstraction of an F atom does not occur easily. This then suggests that a comparison of the extinguishment effectiveness of HCF_3 with the extinguishment effectiveness of CF_4 should yield useful information as to the potential role of the ·CF_3 radical. If the differences in effectiveness are significant and cannot be explained in terms of small differences in heat capacities, then it would be reasonable to conclude that the ·CF_3 radical does make a significant contribution as a "chemical catalytic" extinguishing agent.

EXPERIMENTAL

The experiments suggested here have been done in our laboratories. In these experiments, the heat removed from the flame is used as measure of the degree of extinguishment, with extinguishment being the point at which no heat is removed by the burner.

The Sapphire 0-4 Burner used in these experiments is a modified laboratory Meker burner (diameter = 3.7 cm). The heat absorbed by the burner is carried off by ethylene glycol, circulated at a measured flow rate by a gear pump through a cooling loop (3/16" copper tubing) silver soldered to the outside of the burner rim. The increase in the temperature of the ethylene glycol is measured by a pair of

thermocouples, located in the cooling loop just below the points of attachment of the loop to the burner rim.

In these experiments, the agent was premixed with methane and "air" (21% O_2, 89% N_2). The flow rates of agent and "air" were fixed, and the flow rate of CH_4 was "scanned" from the lean extinguishment limit to the rich extinguishment limit. At each value of the fuel-air equivalence ratio, ϕ, the inhibited flame was compared with an identical (except for the absence of the agent) uninhibited flame.

RESULTS

Figure 1 compares the uninhibited flame with flames inhibited by the same amounts of CF_4 and HCF_3. It is immediately noted that HCF_3 removes very little heat from lean flames, while CF_4 extinguishes these flames; conversely, fuel-rich flames are extinguished by HCF_3, but not by CF_4.

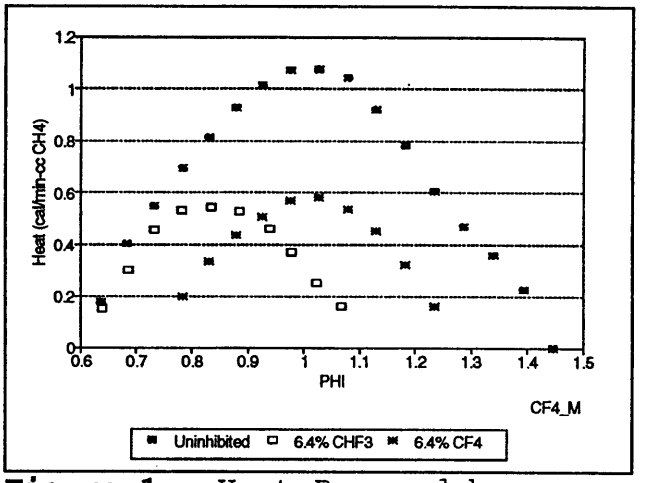

Figure 1. Heat Removed by Burner

Figure 2 plots these data in a different fashion, and illustrates the regions in which each agent is the more effective. In this figure, the energy absorbed by the burner from an uninhibited flame is once again displayed. Superimposed for each agent is a data set which shows the magnitude by which the agent reduces the amount of heat absorbed by the burner. This reduction in the amount of heat absorbed by the burner is a combination of two factors: cooling due to the heat capacity of the agent, and inhibition of the flame chemistry due to the fact that fewer molecules (in the cooler flame) have adequate energy to surmount the activation energy barrier. It can be shown by a straightforward heat balance that the second of these two factors is by far the larger. It is evident from Figure 2 that CF_4 is nearly equally effective at all values of ϕ, while HCF_3 has very little effect on lean flames, but has a larger effect than CF_4 on rich flames.

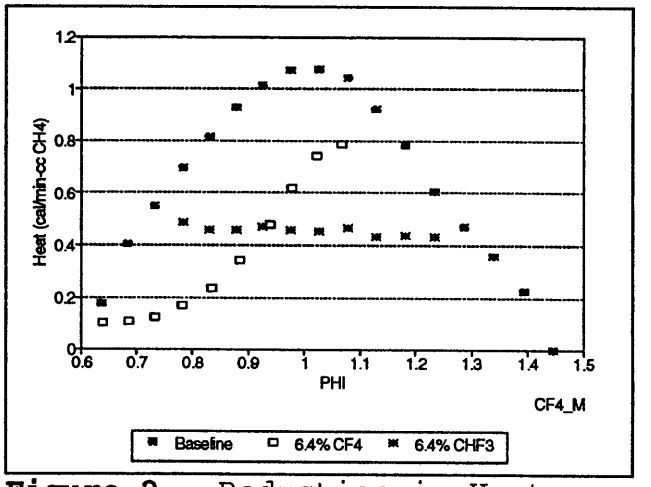

Figure 2. Reduction in Heat Absorbed by Burner

It is proposed that these differences can be explained simply in terms of the "fuel content" of HCF_3 as illustrated by the following overall stoichiometry.

$$2\ HCF_3 + 2\ H_2O + O_2 \rightarrow 6\ HF + 2\ CO_2 \qquad (4)$$

This equation suggests that some of the oxygen is used in combustion of the HCF_3 and that the fuel-air equivalence ratio, ϕ, for combustion of CH_4 should be altered to reflect the availability of less oxygen. When this is done, Figure 3 is obtained. In this figure, the heat absorbed by the burner as a function of ϕ is seen to be nearly identical for both agents. This finding is consistent with a model in which the dominant mechanisms of the two agents are both the same (physical); HCF_3 does alter the chemistry of the flame (but only to the degree that it serves as a fuel). The heat capacities of these two agents differ by less than 5% at typical flame temperatures, with CF_4 having the greater heat capacity.

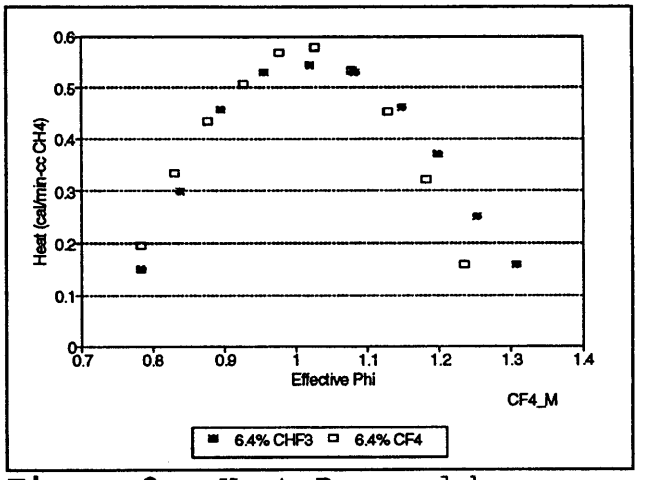

Figure 3. Heat Removed by Burner; ϕ Adjusted for Consumption of O_2 by HCF_3

CONCLUSION

There is no persuasive evidence for the hypothesis that the $\cdot CF_3$ radical might be serving as a "catalytic chemical" agent. Needless to say, this "back-of-the-envelope" argument needs to be substantiated by careful modeling. Moreover, it would be of value to test this conclusion on another pair of compounds such as C_2F_6 and C_2HF_5.

ACKNOWLEDGEMENTS

The principal authors gratefully acknowledge the work of the two undergraduate students who contributed to this work. Justin Schiro was the 1995 NSF REU student who suggested and conducted the first experiments in our laboratories in which ϕ is scanned for a fixed amount of added extinguishing agent. Chris Spencer is still working with us and made all the careful measurements reported here.

This work was supported by the Air Force Office of Scientific Research, Contract No. F49620-94-1-0241.