

# EFFECT OF INHIBITOR CONCENTRATION ON THE INHIBITION MECHANISM OF FLUOROMETHANES IN PREMIXED METHANE-AIR FLAMES

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## Abstract

The mechanisms of inhibition of premixed methane-air flames in the presence of difluoromethane, trifluoromethane, and tetrafluoromethane are studied. The chemistry of these agents is expected to be similar to that of agents which may be used as replacements for  $\text{CF}_3\text{Br}$ . The burning rates of premixed methane-air flames stabilized on a Mache-Hebra nozzle burner are determined using the total area method from a schlieren image of the flame. The three inhibitors are tested over an initial mole fraction from 0 to 8% at nominal values of the fuel-air equivalence ratio,  $\phi$ , equal to 0.9, 1.0, and 1.1. The measured burning rate reductions are compared with those predicted by numerical solution of the mass, species, and energy conservation equations employing a detailed chemical kinetic mechanism recently developed at the National Institute of Standards and Technology (NIST). Even in this first test of the kinetic mechanism on inhibited hydrocarbon flames, the numerically predicted burning rates are in excellent agreement for  $\text{CH}_2\text{F}_2$  and  $\text{CF}_4$  and within 35% for  $\text{CF}_3\text{H}$ . The effects of inhibitor concentration on the decomposition pathway of the inhibitors and on the H, O, and OH radical production and consumption rates are discussed. The modified decomposition pathway and the reduced radical consumption explain the diminishing effectiveness of  $\text{CF}_3\text{H}$  and  $\text{CH}_2\text{F}_2$  at higher concentrations.

## Introduction and Background

Because of its destruction of stratospheric ozone, production of the widely used and efficient [1] fire suppressant halon 1301 ( $\text{CF}_3\text{Br}$ ) has been discontinued, and a number of alternate agents have been proposed [2]. Since these agents are not as effective as  $\text{CF}_3\text{Br}$ , there exists a need to understand the mechanism of inhibition and suppression of these proposed alternatives (mostly fluorinated hydrocarbons and perfluorinated alkanes) to help guide the search for more effective agents. This article describes measurements and numerical calculations of the reduction in burning rate of premixed methane-air flames with the addition of three fluoromethanes ( $\text{CF}_4$ ,  $\text{CF}_3\text{H}$ , and  $\text{CH}_2\text{F}_2$ ) which demonstrate some of the characteristics of the alternatives, while having structures simple enough so that their chemistry can be described by a recently developed kinetic mechanism.

Early studies [3-9] of the inhibitory effect of halogenated hydrocarbons on flames were conducted in premixed systems. The premixed laminar burning rate is a fundamental parameter describing the overall reaction rate, heat release, and heat and mass transport in a flame. In addition, the reduction in the premixed flame burning rate is useful for understanding the mechanism of chemical inhibition of fires since diffusion flames often have a stabilization region which is premixed, and good correlation has been found between the reduction in burning rate and the concentration of inhibitors found to extinguish diffusion flames [10]. Premixed flame burners have flow fields which are relatively easily characterized, making interpretation of the inhibitor's effect on the overall reaction rate straightforward.

higher hydrogen to fluorine ratio in the fuel and the decomposition pathway which proceeds through the species CHF and CHF<sub>2</sub>. Tetrafluoromethane is an example of a perfluorinated agent. These compounds have been argued to be inert (due to the absence of the hydrogen atom which is more easily abstracted than a fluorine). The present research provides burning rate data useful for a first examination of the performance of the NIST fluorinated-species kinetic mechanism in hydrocarbon flames, and examines the mechanisms of inhibition implied by this mechanism as a function of initial inhibitor mole fraction for these three fluoromethanes.

## Experiment

Numerous techniques exist for measuring burning rates of flames, and there are good reviews in the literature [26,27]. All of the flame and burner geometries employed, however, cause deviations from the desired one-dimensional, planar, adiabatic flame. In the present research, a premixed conical Bunsen-type nozzle burner is used. The low rate of heat loss to the burner, the low strain rate, and the low curvature facilitate comparisons of the experimental burning rate with the predictions of a one-dimensional numerical calculation of the flame structure. The burning rate in Bunsen-type flames is known to vary at the tip and base of the flame and is influenced by curvature and stretch (as compared to the planar burning rate); however, these effects are most important over small regions of the flame. Although measurement of a true one-dimensional, planar, adiabatic burning rate is difficult, 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. For comparison with the results of other researchers, the absolute burning rates of the uninhibited flames are also presented.

The flame speed measurements are performed using a Mache-Hebra nozzle burner [28]. The burner consists of a quartz tube 27 cm long with an area contraction ratio of 4.7 and a final nozzle diameter of  $1.02 \pm 0.005$  cm. The nozzle contour is designed to produce straight-sided schlieren and visible images which are very closely parallel. The burner is placed in a square acrylic chimney 10 cm wide and 86 cm tall with provision for co-flowing air or nitrogen gas (for the present data, the co-flow velocity is zero). Gas flows are measured with digitally-controlled mass flow controllers (Sierra Model 860\*\*) with a claimed repeatability 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 inhibitors are trifluoromethane (Dupont), tetrafluoromethane (PCR), and difluoromethane (Allied Signal). House compressed air (filtered and dried) is used after it has been additionally cleaned by passing it through an 0.01 micron filter, a carbon filter, and a desiccant bed to remove small aerosols, organic vapors, and water vapor. The product gas temperature of the uninhibited flames is measured with Pt/Pt 6% Rh - Pt/Pt 30% Rh thermocouples which are coated with yttrium oxide to reduce catalytic reaction on the thermocouple surface. Measurements with two bead diameters (344 and 139  $\mu\text{m}$ ) allow correction for radiation losses.

For the present data, the visible flame height is maintained at constant value of 1.3 cm to provide similar rates of heat loss to the burner, while the desired equivalence ratio and inhibitor concentration are preserved. An optical system provides simultaneously the visible and

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\*\* 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.

schlieren images of the flame. A 512 by 512 pixel CCD array captures the image which is then digitized by a frame-grabber board in an Intel 486-based computer. The flame area is determined (assuming axial symmetry) from the digitized schlieren image using image processing software. The average mass burning rate for the flame is determined using the total area method [27]. The experimental technique is similar to that used extensively by Van Wouterghem and Van Tiggelen [29]. The present burner, however, is larger, is not water-cooled, and the material (quartz) has a much lower thermal conductivity than that in ref. [29].

## Model

The structure of the inhibited premixed methane-air flame was calculated using currently available techniques [30-32]. The equations of mass, species, and energy conservation were solved numerically for the initial gas compositions of the experiments. The solution assumes isobaric, adiabatic, steady, planar, one-dimensional, laminar flow and neglects radiation and the Dufour effect (concentration gradient-induced heat transfer) but includes thermal diffusion. The adopted boundary conditions, corresponding to a solution for a freely-propagating flame, are a fixed inlet temperature of 298 K with specified mass flux fractions at the inlet and vanishing gradients downstream from the flame. The calculations employed a chemical kinetic mechanism recently developed at NIST [2, 33-35] for fluorine inhibition of hydrocarbon flames. Several reactions were modified in the present calculations to represent more recent estimations [36]. The reactions which were modified are:  $\text{CF}_3 + \text{F} = \text{CF}_4$ ,  $\text{CO} + \text{F} + \text{M} = \text{CF}_2\text{O} + \text{M}$ , and  $\text{CF}_2\text{O} + \text{H} = \text{CF}_2 + \text{H}_2\text{O}$ , and the new expressions for the specific reaction rate constants are:  $4.00 \times 10^{13} \text{ T}^{-0.2}$ ,  $1.03 \times 10^{19} \text{ T}^{-1.4} e^{-245/T}$ , and  $5.50 \times 10^8 \text{ T}^{-1.4} e^{-9600/T}$ , respectively ( $\text{cm}^3\text{-mole-sec}$  units). It should be noted that these rates were not modified to promote agreement with the experimental results and that these changes produce only about a one percent modification to the calculated burning rates for the present conditions. The 85-species mechanism uses a hydrocarbon sub-mechanism and adds  $\text{C}_1$  (200 reactions) and  $\text{C}_2$  (400 reactions) fluorochemistry. The hydrocarbon sub-mechanism has been updated, in the present work, to use GRIMECH (31 species, 177 reactions; [37]) which more closely predicts our experimental uninhibited burning rates. Although all of the reactions are not necessary to adequately describe the present flames, the comprehensive full mechanism was used for these initial calculations. Reduction of the mechanism will be performed later after more experimental validation. It should be emphasized that the mechanism adopted [33-36] for the present calculations should be considered only as a starting point. Numerous changes to both the reactions incorporated and the rates may be made once a variety of experimental and theoretical data are available for testing the mechanism.

## Results

The radiation-corrected temperature of the uninhibited flames was measured at 4 mm above the flame tip to be 2054, 2075, and 2050 K for  $\phi=0.95$ , 1.0, and 1.05 respectively, while the adiabatic flame temperature is calculated to be 2191, 2229, and 2234 K (note that the inhibited flame speeds themselves were measured for a slightly wider range of equivalence ratio, 0.9 to 1.1. In these experiments, the measured final temperatures are about 150 K lower than the calculated adiabatic flame temperatures. Heat losses to the burner, although important near the rim, are not expected to be large compared to the heat release integrated over the entire flame. The observed heat loss may be due to non-one-dimensional effects, radiation, or chemical non-equilibrium in the post-combustion gases. Nonetheless, since the temperature difference is not too great, it seemed most appropriate to model the flame as freely-propagating

rather than burner-stabilized (where heat losses, for example in a flat flame burner, are typically much greater).

Figure 1 presents the measured mass burning rate (expressed as the equivalent flame velocity for flame propagation into reactants at 298 K) as a function of equivalence ratio for the uninhibited methane-air flame. For values of  $\phi$  from 0.8 to 1.2 the data are within 5% of the results of Law [38] and of the numerical calculations. The agreement between the experiment and model is quite good. This is expected since GRIMECH is being developed using existing experimental methane-air burning rates and the present experimental results are close to those of other researchers.

The results for the flames inhibited by  $\text{CF}_4$ ,  $\text{CH}_2\text{F}_2$ , and  $\text{CF}_3\text{H}$  are presented in Figs. 2a-2c respectively. The figures show the burning rate of the inhibited flame (normalized by the burning rate of the uninhibited flame) for values of  $\phi$  of 0.9, 1.0, and 1.1 (here, the equivalence ratio is calculated based on the oxygen demand of the fuel only). Experimental and numerical results are presented for inhibitor mole fractions up to 0.08 when possible; for the lean stoichiometry and the inhibitors  $\text{CF}_4$  and  $\text{CF}_3\text{H}$ , flames could not be stabilized for inhibitor mole fractions above about 4%. Most of the scatter in the plots of the experimental burning rate results from flame fluctuations: the camera framing rate is 30 Hz and flame area is obtained from a single image; signal averaging would reduce this scatter.

Figure 2a shows the results for  $\text{CF}_4$ . The experiments show slightly more inhibition for richer flames as does the model. The calculated burning rate is in excellent agreement with the numerical solution. Figure 2b presents the results for  $\text{CH}_2\text{F}_2$ . Again, rich flames show more inhibition than the lean flames but the effect is large for  $\text{CH}_2\text{F}_2$ . The fuel effect of adding  $\text{CH}_2\text{F}_2$  to lean flames increases the adiabatic flame temperature above the uninhibited case for low  $\text{CH}_2\text{F}_2$  mole fractions, promoting a higher burning rate. In competition with this effect is the slower kinetics caused by presence of the fluorine compounds as discussed below. Note that although the adiabatic flame temperature is higher for lean flames with up to 5%  $\text{CH}_2\text{F}_2$ , the burning rate is still reduced relative to the uninhibited flame. The results for  $\text{CF}_3\text{H}$  are shown in Fig. 2c. The mechanism is showing the proper qualitative features of the inhibition including the dependence on stoichiometry and the reduced inhibitory effect at higher inhibitor mole fractions; however, the calculation is showing up to 35% more reduction in burning rate than is observed in the experiments.

## Discussion

The results for  $\text{CF}_4$  are not discussed in detail because examination of the reaction fluxes indicates that over the primary reaction region of the flame, the fluorinated-species reactions did not significantly affect the production or consumption of H, O, or OH. Although about 10% of the  $\text{CF}_4$  does decompose near the primary reaction zone of the flame, most of the calculated decomposition is far downstream and fluorinated-species reactions do not significantly affect the burning rate. Rather, the effect of  $\text{CF}_4$  is mostly to lower the heat release per unit mass of the reactants and consequently reduce the burning rate.

Previous researchers have suggested [16,22,23,25] that the overall reaction rate in premixed flames is reduced with addition of fluorinated compounds through their (and their decomposition products') reaction with hydrogen atom to form less reactive radicals and HF. Figures 2b and 2c indicate a decreasing inhibition effect with initial inhibitor mole fraction in both the experiments and the calculations for stoichiometric flames. Two approaches are used to examine this phenomenon. The numerically calculated reaction fluxes of H, O, and OH are examined here to determine the effect of increasing inhibitor mole fraction on the production and consumption of these radicals by reactions involving fluorine. Also, the consumption

pathways of the inhibitor and its fragments are examined to determine changes that occur at the higher inhibitor concentrations.

Figure 3a shows the fraction of the total radical production ( $^+$  superscript) and consumption ( $^-$  superscript) for H, O, and OH by reactions involving fluorine for inhibition by  $\text{CH}_2\text{F}_2$ . The largest effect is for hydrogen atom. The H-atom consumption increases at higher  $\text{CH}_2\text{F}_2$  concentrations, but at a decreasing rate with increasing inhibitor concentration. The H-atom production rate, however, increases with increasing  $\text{CH}_2\text{F}_2$  concentration. Examination of the numerical results shows that the consumption of H-atom by the species  $\text{CHF}\cdot\text{O}$ ,  $\text{CF}\cdot\text{O}$ , and  $\text{CHF}_2$  does not increase proportionately as the  $\text{CH}_2\text{F}_2$  concentration increases from 4 to 8%, whereas the reactions producing H-atom,  $\text{H}_2 + \text{F} = \text{H} + \text{HF}$ , and  $\text{CF} + \text{H}_2\text{O} = \text{CHF}\cdot\text{O} + \text{H}$ , increase faster than the inhibitor increase. As Fig. 3a shows, the net H-atom consumption rate is approximately constant between 6 and 8%  $\text{CH}_2\text{F}_2$ . The results for O- and OH-atom are even more pronounced: the consumption rates are approximately constant for  $\text{CH}_2\text{F}_2$  mole fractions from 4 to 8% while the production rates of these radicals increase more rapidly over this range than they do for  $\text{CH}_2\text{F}_2$  initial mole fractions from 0 to 4%. Between 4 and 8%  $\text{CH}_2\text{F}_2$ , the net OH-atom consumption rate is constant, and the net O-atom production rate increases, so that there is a decrease in the sum of the H, O, and OH consumption rates from 6 to 8%  $\text{CH}_2\text{F}_2$ . The fluorine atom concentration remains low, 2, 8, and 2 ppm at 0.5, 4.0 and 8.0%  $\text{CH}_2\text{F}_2$  respectively. It is useful to note that the decrease in the net radical consumption does not occur until the  $\text{CH}_2\text{F}_2$  initial mole fraction reaches just above 6%. This is also the approximate concentration at the inflection point in the burning rate for  $\phi=1.0$  in Fig. 2b. As discussed below, changes in the radical consumption rate for  $\text{CF}_3\text{H}$  occur at an inhibitor mole fraction of approximately 4%.

As illustrated in Fig. 3b, the results for  $\text{CF}_3\text{H}$  are similar for H-atom reaction fluxes. The H-atom consumption increases at higher  $\text{CF}_3\text{H}$  concentrations, but at a slightly decreasing rate with increasing inhibitor concentration (due to the lower H-atom concentrations at higher  $\text{CF}_3\text{H}$  concentrations). In contrast, the H-atom production rates increase faster than the inhibitor initial mole fraction does (again from the reactions:  $\text{H}_2 + \text{F} = \text{H} + \text{HF}$ , and  $\text{CF} + \text{H}_2\text{O} = \text{CHF}\cdot\text{O} + \text{H}$ ). The net H-atom consumption increases only slightly from 4 to 8%  $\text{CF}_3\text{H}$ . The net effect for both O and OH is small: reactions involving fluorinated species do not have a large effect on the net consumption of O and OH radicals for  $\text{CF}_3\text{H}$  concentrations up to 8%. Fluorine atom concentrations again remain low, 3, 17, and 13 ppm at 0.5, 4.0 and 8.0%  $\text{CH}_2\text{F}_2$  respectively.

Figures 4a, b show the dominant reaction pathways for  $\text{CH}_2\text{F}_2$ , and  $\text{CF}_3\text{H}$  for  $\phi=1$  as deduced from the numerical calculations. The reaction fluxes are integrated only over the primary reaction zone of the flame (here selected to be the domain encompassing fuel and CO consumption). The arrows connect species of interest; next to the arrows are the second reacting species. The percentage of the first reactant which goes through that route is listed from top to bottom for inhibitor initial mole fractions of 2, 4, 6, and 8% respectively. From this figure we can observe the changes in the reaction pathway of the inhibitor as a function of its initial mole fraction. As shown in Fig. 4a, about 82% of the initial breakdown of  $\text{CH}_2\text{F}_2$  at low concentrations is calculated to be due to H and OH radical attack, while about 15% is due to thermal decomposition. In contrast, at 8%  $\text{CH}_2\text{F}_2$ , reaction with H-atom is about the same, reaction with OH decreases from 50 to 22%, and thermal decomposition accounts for 44% of the  $\text{CH}_2\text{F}_2$  destruction. The change in the consumption of  $\text{CHF}\cdot\text{O}$  and  $\text{CF}\cdot\text{O}$  with higher inhibitor loading is similar: the H-atom reaction is reduced moderately and destruction by thermal decomposition is two or three times higher. Formation of two-carbon fluorinated species (for clarity, not shown), from  $\text{CHF}_2$  reaction with  $\text{CH}_3$ , is estimated to increase from 21 to 39% of the  $\text{CHF}_2$  consumption for 2 and 8%  $\text{CH}_2\text{F}_2$  respectively; while  $\text{CHF}_2$  reaction with

O and OH decreases by a factor of three, and reaction with H decreases only 20%. Interestingly, the consumption of CH is predicted to dramatically change. At low inhibitor loading, reaction with  $O_2$ ,  $H_2O$  and other stable species is dominant, as in uninhibited flames. At 2%  $CH_2F_2$ , 24% of the CH is predicted to react with HF, while at 8%, this fraction is 57%.

The decomposition route calculated for  $CF_3H$  shown in Fig. 4b also indicates an increasing importance for thermal decomposition reactions as the inhibitor initial mole fraction increases from 2 to 8%. Reactions of trifluoromethane with OH and H decrease by about a third, while thermal decomposition increases from 0 to 33% of its destruction. Likewise, reactions of  $CHF:O$  and  $CF:O$  with H- and OH-atom decrease by about a factor of two, while thermal decomposition of these species more than doubles. Reaction pathways for  $CF_2$ ,  $CF$ , and  $CF_3$  are about the same, although reactions of  $CH_3$  with the latter increase from 22 to 31%, so that, again, more two-carbon fluorinated species are formed at the higher inhibitor loading.

## Conclusions

The reduction in burning rate has been determined experimentally and numerically for the inhibitors  $CF_3H$ ,  $CH_2F_2$ , and  $CF_4$  in near-stoichiometric premixed methane-air flames at initial inhibitor mole fractions of 0 to 8%. Even at this early stage of development, the NIST fluorine-inhibition mechanism predicts the burning rate reduction quite well for these flames.

The numerical results have been used to examine the effects of increasing inhibitor concentration on the inhibition mechanism. A decrease in the effectiveness of the inhibitors at higher concentrations is observed for all three agents both in the experiments and in the numerical calculations. Examination of the numerical solutions indicates that for  $CH_2F_2$  and  $CF_3H$ , consumption of the inhibitor and inhibitor fragments by radical attack is favored at low concentrations, while at inhibitor concentrations approaching 8%, thermal decomposition reactions become more important. Below about 5% inhibitor, reactions involving fluorinated species cause a net increase in the consumption rate of H, O, and OH, while above 5%, there is little additional radical consumption by these reactions.

Further research is necessary to test the mechanism using data from other experimental configurations. As the mechanism is further developed and refined, even closer agreement for  $CF_3H$ -inhibition of methane-air flames should be possible, and the mechanism can be extended to larger fuels and inhibitors.

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## Figure Captions

Figure 1 - Experimental burning rate (symbols) of the premixed methane-air flame in the nozzle burner as a function of fuel-air equivalence ratio, and the numerically calculated burning rate (solid line).

Figures 2a, 2b, and 2c - Burning rate normalized by the uninhibited burning rate at the same stoichiometry for the methane-air flame at fuel-air equivalence ratios of 0.9, 1.0, and 1.1 as a function of the inhibitor mole fraction for  $\text{CF}_4$ ,  $\text{CH}_2\text{F}_2$ , and  $\text{CF}_3\text{H}$ . The symbols present the experimental data, the solid lines the results of the numerical calculation.

Figure 3a, b - Numerically calculated hydrogen, oxygen, and hydroxyl radical production and consumption rates from reactions involving fluorinated species as a function of initial inhibitor mole fraction for  $\text{CH}_2\text{F}_2$  and  $\text{CF}_3\text{H}$ .

Figure 4a,b - Dominant reaction pathways for decomposition of the inhibitors  $\text{CH}_2\text{F}_2$  and  $\text{CF}_3\text{H}$  in a stoichiometric premixed methane-air flame. The fraction of the first reactant that goes through a particular reaction path for 2, 4, 6, and 8% inhibitor is listed from top to bottom next to the arrow for the path.



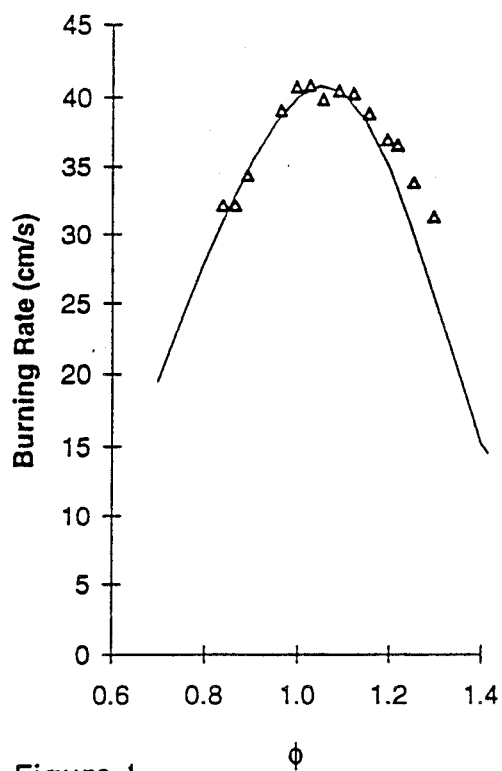


Figure 1

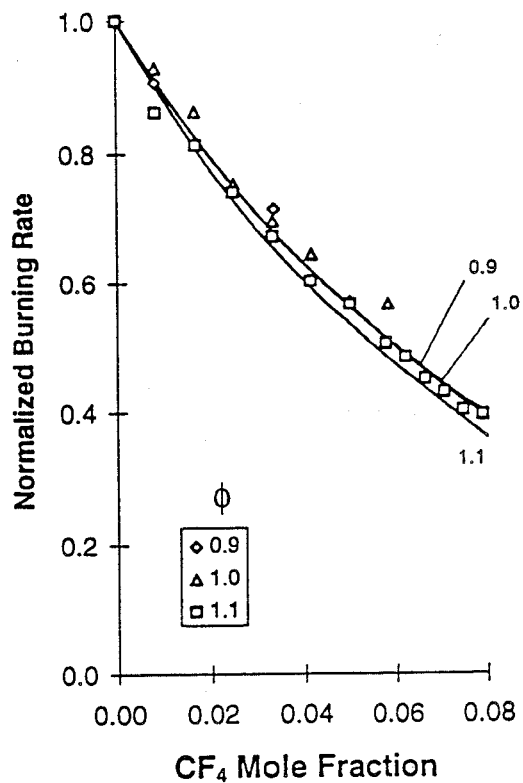


Figure 2a

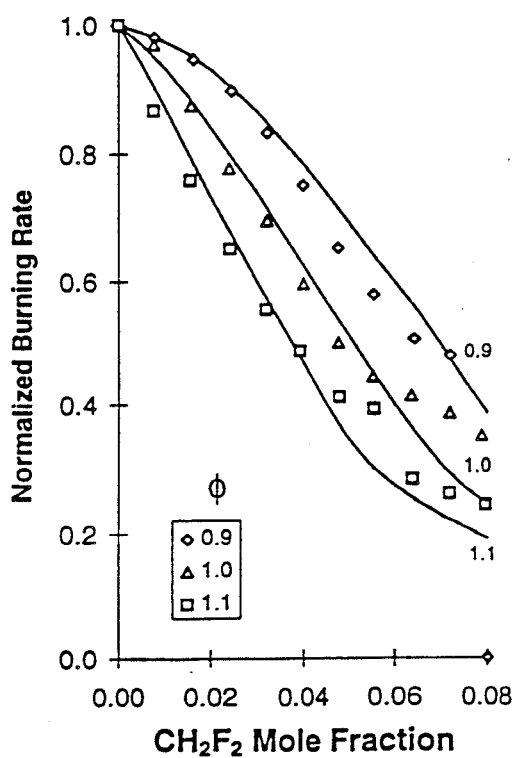


Figure 2b

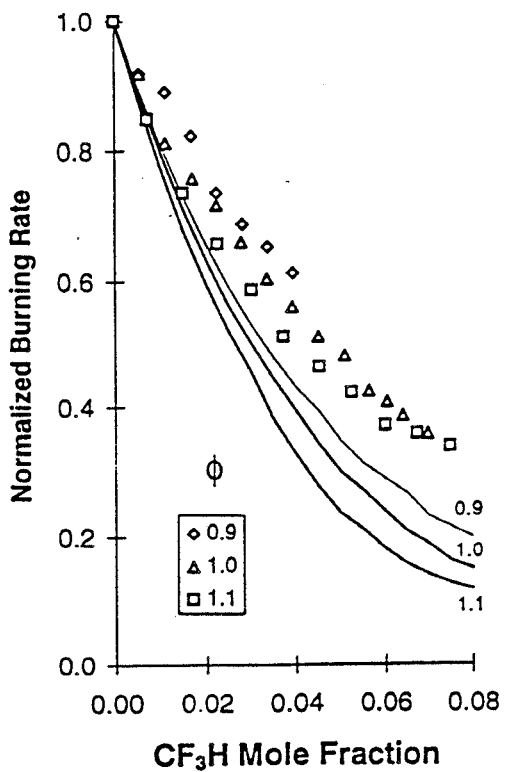


Figure 2c

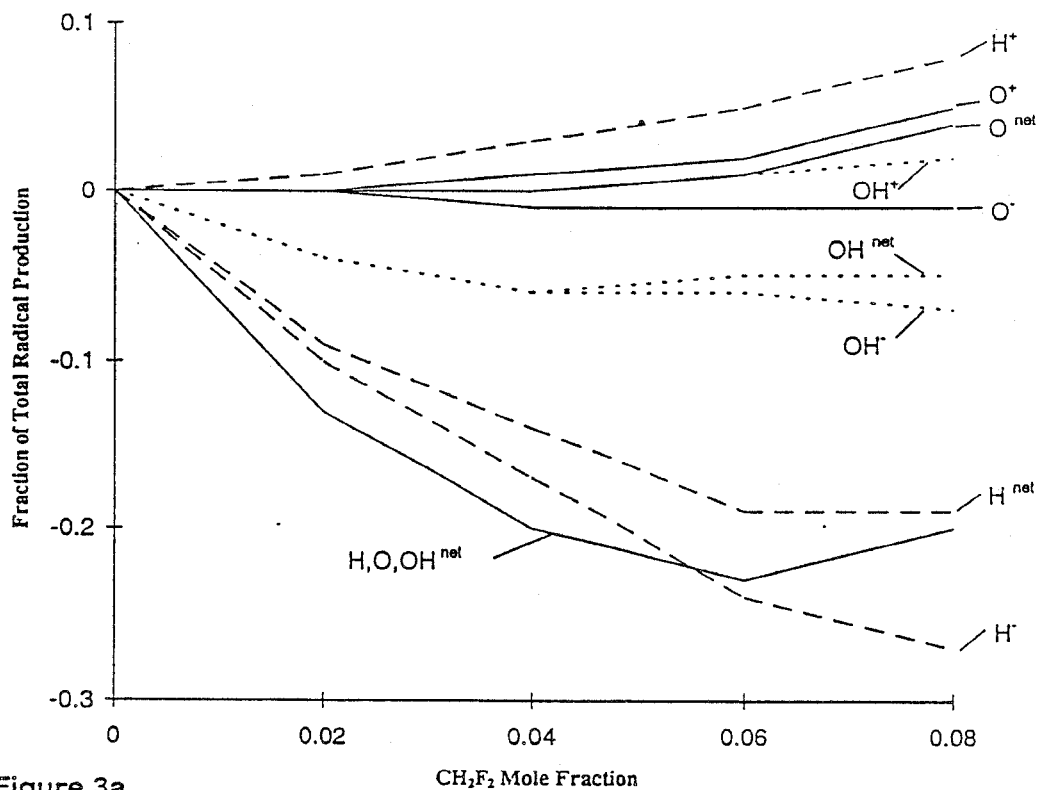


Figure 3a

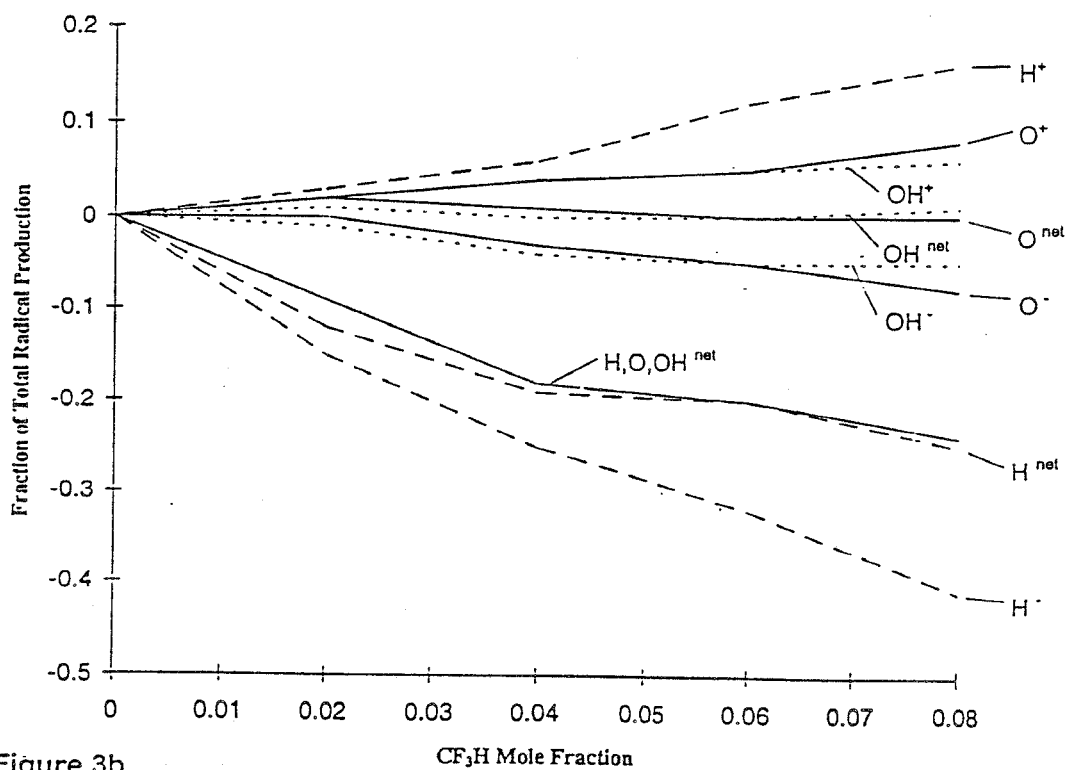


Figure 3b



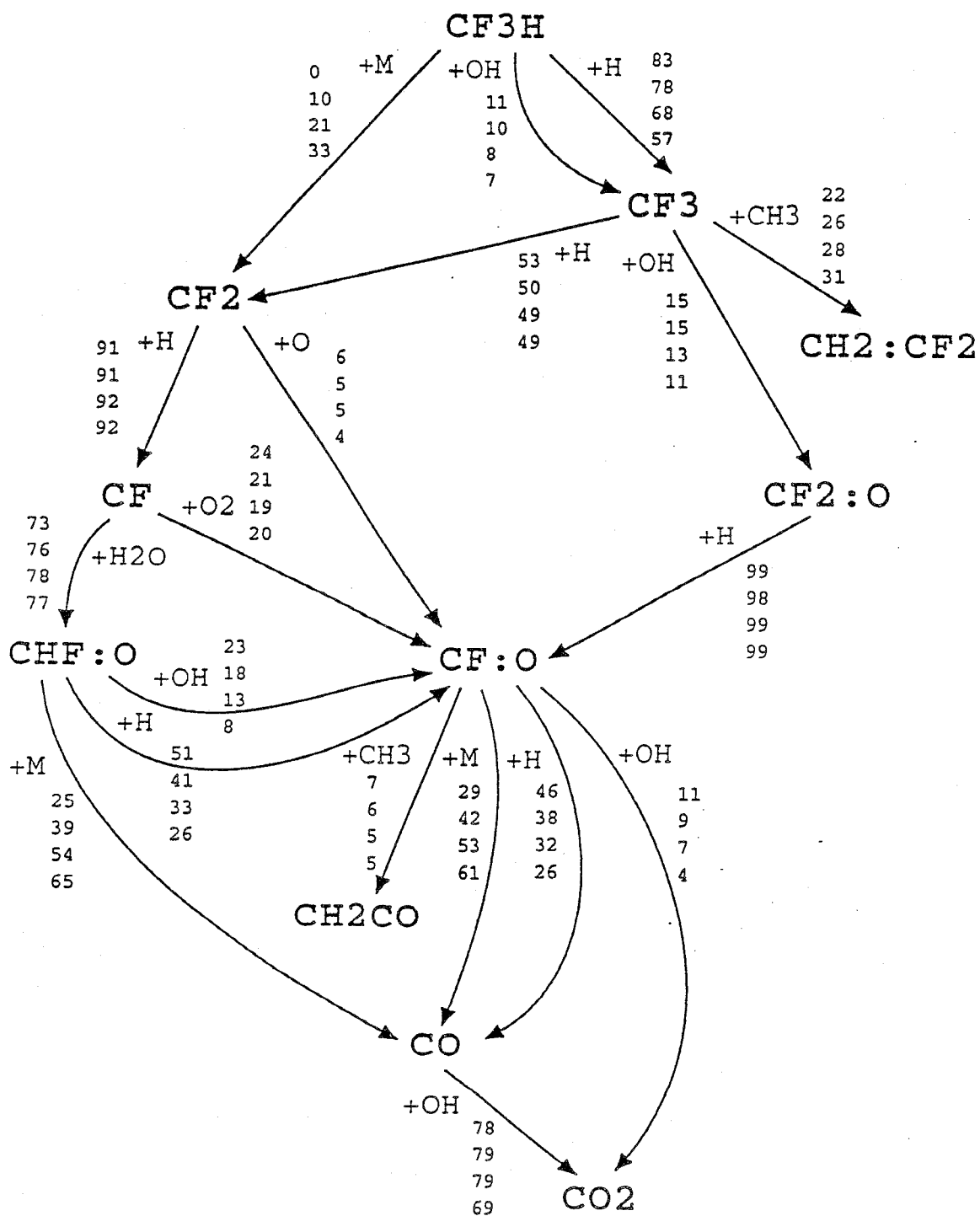


Figure 4b