INHIBITION OF PREMIXED METHANE-AIR FLAMES BY HALON ALTERNATIVES

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Abstract

Halogenated hydrocarbons are effective and widely used as fire suppressants. Because of their suspected destruction of stratospheric ozone, however, the production of these agents, the most popular being halon 1301 (CF_3Br), has been discontinued. There exists a need to develop alternatives to the halons, to establish the relative effectiveness of alternative inhibitors, and to understand the mechanism of inhibition of the new agents. The agents which are currently being considered are mostly fluorinated alkanes. This article describes the first measurements of the reduction in burning rate of premixed methane-air flames inhibited by the two-carbon fluorinated species C_2F_6, C_2HF_5, $C_2H_2F_4$ and the three-carbon species C_3F_8 and C_3HF_7, all of which are being considered as replacements to CF_3Br. The burning rate of premixed methane-air flames stabilized on a Mache-Hebra nozzle burner is determined using the total area method from a schlieren image of the flame. The inhibitors are tested over a range of concentration and fuel-air equivalence ratio, ϕ. The measured burning rate reduction caused by addition of the inhibitor is compared (for the two-carbon species) with that 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).

Introduction and Background

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. 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 for the inhibitors C_2F_6, C_2HF_5, $C_2H_2F_4$, C_3F_8, and C_3HF_7.

Experiment and Model

The flame speed measurements are performed using a Mache-Hebra nozzle burner [11] which has been described previously [12-14] 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 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 laboratory 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 [15].

The structure of the inhibited premixed methane-air flame was calculated using currently available techniques [16-18]. 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 calculations employed a chemical kinetic mechanism recently developed at NIST [2, 19-21] for fluorine inhibition of hydrocarbon flames. Several reactions were modified in the present calculations to represent more recent estimations [22]. The reactions which were modified are: $CF_3 + F = CF_4$, $CO + F + M = CF{:}O + M$, and $CF_2{:}O + H = CF{:}O + HF$, and the new expressions for the specific reaction rate constants are: $4.00 \times 10^{13}\ T^{-0.2}$, $1.03 \times 10^{19}\ T^{-1.4}\ e^{-245/T}$, and $5.50 \times 10^{8}\ T^{-1.4}\ e^{-9600/T}$, respectively ($cm^3$-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 C_1 (200 reactions) and C_2 (400 reactions) fluorochemistry. The hydrocarbon sub-mechanism has been updated, in the present work, to use GRIMECH (31 species, 177 reactions; [23]) which more closely predicts our experimental uninhibited burning rates. Calculations were performed only for the two-carbon inhibitors. In one calculation method, the agent is treated as an inert species, while in the other, full chemical reaction of the inhibitor is permitted. 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 and Conclusions

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 ϕ 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.

Figures 2a,b,c present the burning rate reduction of caused by addition of the inhibitors C_2F_6, C_2HF_5, and $C_2H_2F_4$. As the figures show, the greatest reduction in burning rate was obtained with the perfluorinated agent C_2F_6, followed by C_2HF_5 and $C_2H_2F_4$. For the agent C_2F_6, the burning rate calculated by assuming the agent to be inert under-predicts the burning rate reduction by about 25%, while the calculation which allows full reaction overpredicts by about 14%. As shown in Figs. 2b and 2c, the results for C_2HF_5 and $C_2H_2F_4$ are similar. An important feature of the inhibition is its dependence on the fuel - air equivalence ratio, with larger burning rate reductions occurring in the richer flames. This dependence on the equivalence ratio becomes greater as the hydrogen content of the inhibitor increases. This feature is not captured by the inert calculations; in fact, they predict the opposite: a small decrease in inhibitor effectiveness as ϕ increases from 0.9 to 1.1. An additional observation, clearly illustrated in Figs. 2 and 3, is that all of the inhibitors show a reduced effectiveness as the inhibitor concentrations increases. This has been observed for one-carbon fluorinated agents and the reasons discussed [14].

The results for the three-carbon fluorinated agents are presented in Figs. 3a and 3b. These agents, C_3F_8 and C_3HF_7, are about as effective, on a volume basis, as the two-carbon inhibitors, and show the same large dependence on the equivalence ratio, and on the inhibitor mole fraction. However, in the case of C_3HF_7, the inhibition effect is strongest in the lean flame, whereas in all other cases the rich flames are inhibited most. The reasons for this are presently unclear but are of great interest.

The reduction in burning rate has been determined experimentally and numerically for the fluorinated inhibitors C_2F_6, C_2HF_5, $C_2H_2F_4$, C_3F_8 and C_3HF_7 in near-stoichiometric premixed methane-air flames at inhibitor concentrations up to 8%. These data and analyses represent the first such measurements

and calculations for these agents, fuel and conditions. The calculations illustrate that these inhibitors are *not* inert in the present flames and show that the burning rate reductions are greater than can be accounted for by inhibitors acting as inert species. Even at this early stage of development, the NIST fluorine-inhibition mechanism predicts the burning rate reduction reasonably well for these flames. Further research is necessary to validate the mechanism with other flames and with more stringent comparisons than burning rate (such as detailed flame structure measurements). As the mechanism is further developed and refined, better agreement 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 C_2F_6, C_2HF_5, and $C_2H_2F_4$. The symbols present the experimental data, the solid lines the results of the numerical calculation allowing full chemistry, and the dotted lines present the results with the inhibitor present but constrained to be inert.

Figure 3a, b - 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 C_3F_8, and C_3HF_7.

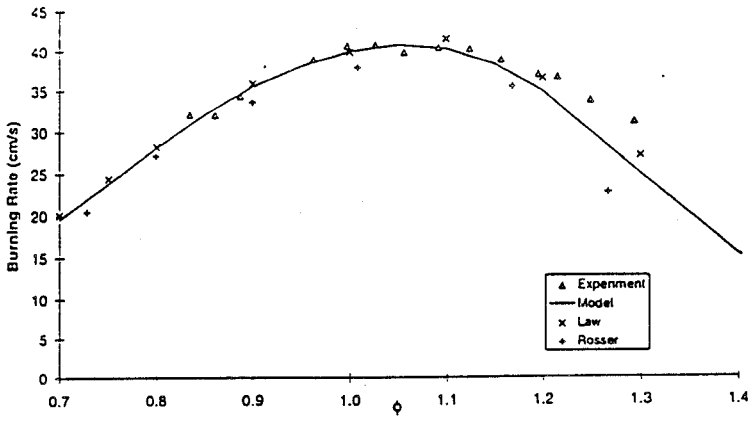

Figure 1

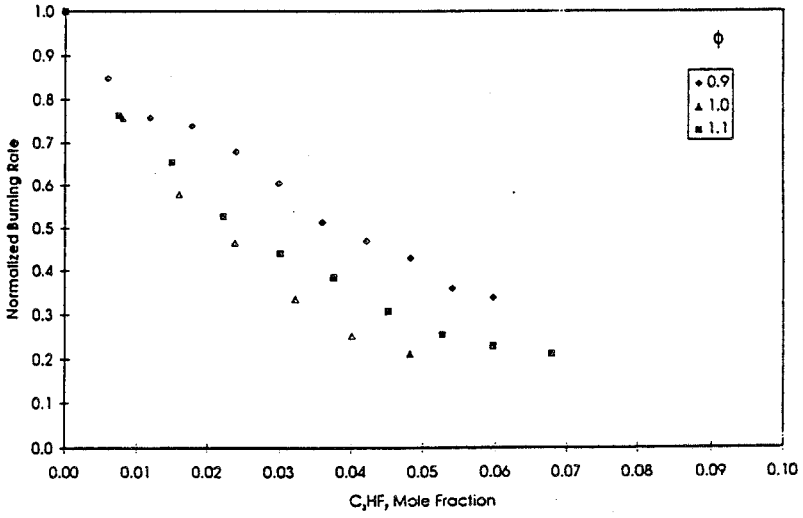

Figure 3a

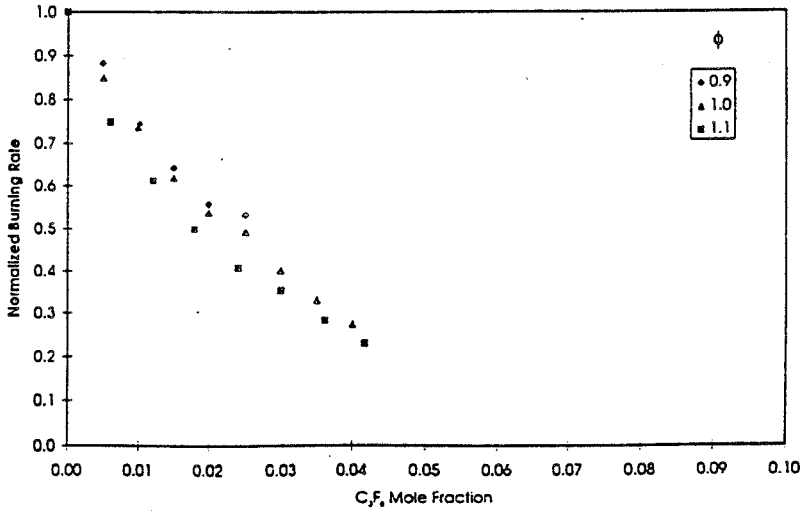

Figure 3b

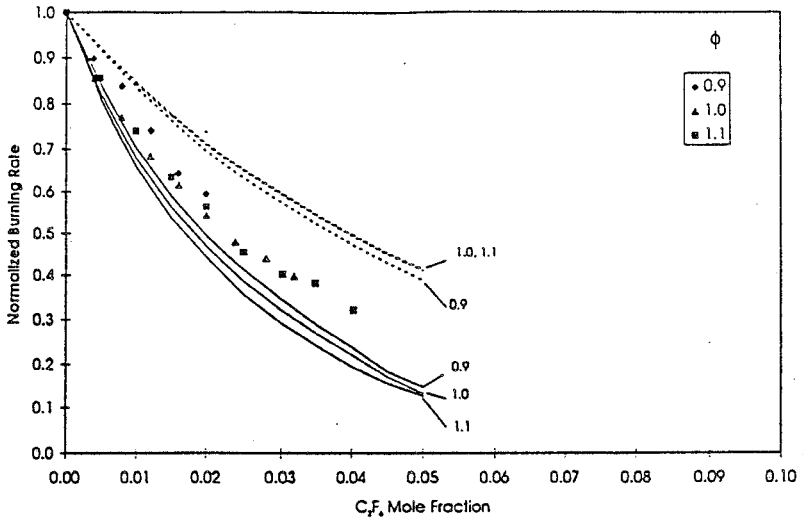

Figure 2a

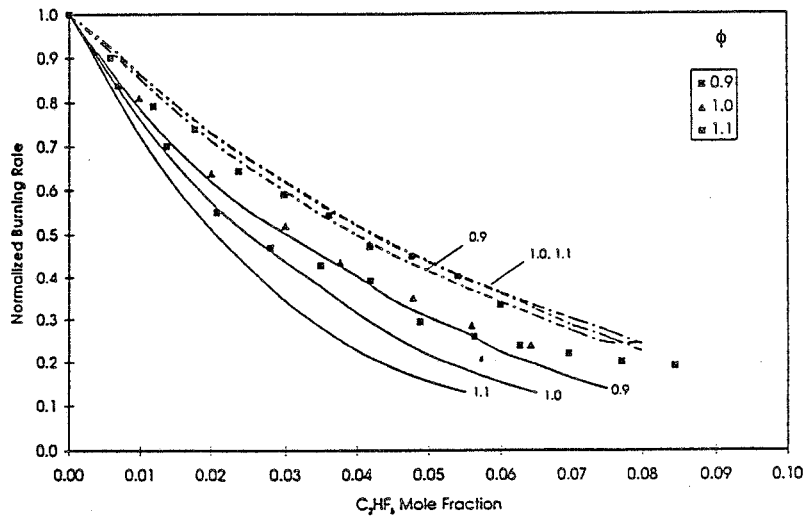

Figure 2b

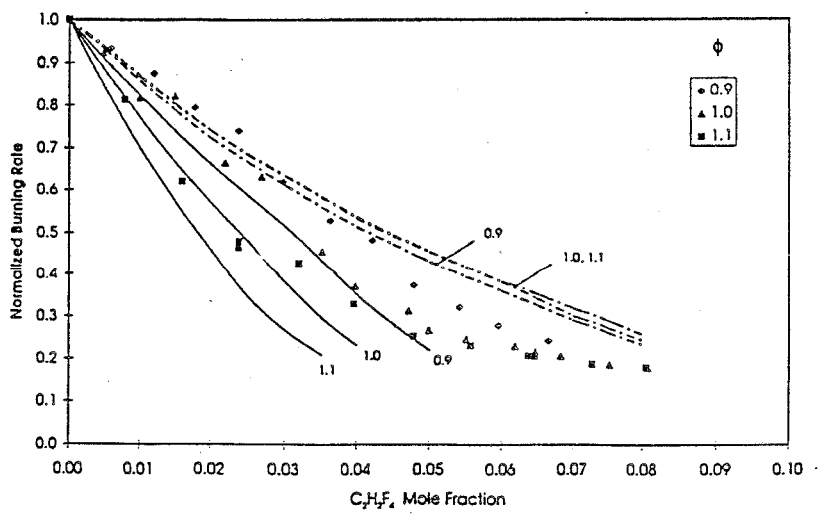

Figure 2c