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EXPERIMENTAL AND NUMERICAL BURNING RATES OF PREMIXED METHANE-AIR FLAMES INHIBITED BY FLUOROMETHANES

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Introduction: The agents which are currently being considered as replacements for fire suppressant agent CF_3Br are mostly fluorinated hydrocarbons and perfluorinated alkanes. This abstract describes measurements of the reduction in burning rate of premixed methane-air flames by the single carbon inhibitors CF_4, CF_3H, and CF_2H_2. Early studies of the inhibitory effects of halogenated hydrocarbons on flames were conducted in premixed systems[1,2,3]. 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[4]. 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 burning rate measurements allow an early assessment of the performance of the NIST fluorinated species chemical kinetic mechanism in premixed flames and are considered to be an initial step in the validation and refinement of the mechanism. The mechanism is being used to gain insight into the possible modes of inhibition of these agents in premixed methane air flames.

Experiment: The flame speed measurements are performed using a Mache-Hebra nozzle burner[5]. 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 ± 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 was 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 are calibrated with bubble and dry (American Meter Co. DTM-200A) flow meters so that their accuracy is ± 1%. 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. Custom-written software controls the flows of air, fuel, and inhibitor necessary for obtaining the constant flame height while preserving the proper values of the equivalence ratio ϕ and inhibitor concentration. An optical system similar to that of Van Tiggelen and co-workers[6,7] was designed to provide simultaneously the visible and schlieren images of the flame. A 512 by 512 pixel CCD array captures the image which is digitized by a frame-grabber board in an Intel 486-based computer. Flame areas are determined from the digital schlieren images (assuming axial symmetry) using custom-written image processing software, and the average mass burning rate for the flame is determined using the total area method[8]. Although measurement of a true one-dimensional, planar, adiabatic burning rate is difficult, the relative change in the burning rate is more robust. Consequently, the inhibited burning rate in the present work is normalized by the uninhibited burning rate. For comparison with the results of other researchers, the absolute burning rate of the uninhibited flames is also presented.

Model The structure of the inhibited premixed methane-air flame is calculated for CF_4, CF_3H, and CF_2H_2 using currently available techniques[9,10,11]. The equations of species and energy conservation are solved numerically for the initial gas compositions of the experiments. The solution assumes isobaric, adiabatic, steady, planar,

*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.

one-dimensional, laminar flow and neglects radiation and the Dufour effect 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 employ a chemical kinetic mechanism recently developed at NIST[12,13] for fluorine inhibition of hydrocarbon flames. The 85-species mechanism employs an existing hydrocarbon sub-mechanism and adds C_1 (200 reactions) and C_2 (400 reactions) fluorochemistry. Fluorinated-species thermochemistry is from the literature when available and is otherwise estimated using empirical methods (such as group additivity) and through application of *ab initio* molecular orbital calculations. Fluorinated species reaction rates from the literature were used when available and these were extended to wider temperature and pressure ranges using RRKM and QRRK methods. Where no rate data were available, rate constants were estimated by analogy with hydrocarbon reactions. Reaction rate constants and thermodynamic data for the hydrocarbon sub-mechanism have been changed, for the present calculations, to those of the more recently developed GRIMECH[14] methane mechanism since it more closely predicts the present experimental uninhibited flame burning rates than the previously used hydrocarbon sub-mechanism.

Results and Discussion: The current data and calculations are extensions of results presented previously[15]; here, the experiments are conducted at a wider range of equivalence ratio and at greater inhibitor mole fractions and also include results for the inhibitor CF_4. 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 flame, together with the results of Rosser *et al.*[2] and Law[16]. For values of ϕ from 0.8 to 1.25 the data are within 5% of the results of Law and of the numerical calculations. The data are about 7% higher than the results of Rosser *et al.*[2] for $\phi < 1.0$ and up to 30% higher for $\phi > 1.0$). The results for the flames inhibited by CF_4, CF_2H_2, and CF_3H are presented in Figures 2 to 4 respectively. The figures show the burning rate of the inhibited flame (normalized by the burning rate of the uninhibited flame) for values of ϕ of 0.9, 1.0, and 1.1 (here, the equivalence ratio is calculated based on the oxygen demand of the fuel only). The numerical results are presented in two ways: the solid lines present solutions which allow full chemistry, while the dotted lines present solutions in which the inhibitor is constrained to be inert so that only the thermal and transport properties of the flame are modified by the inhibitor. Experimental results are presented for inhibitor mole fractions up to 0.08. As Figures 2 to 4 indicate, the measured burning rate reduction for the three inhibitors is a function of the nominal stoichiometry and is greater for richer flames, especially for CF_2H_2. The numerical calculations were preformed for the same range of inhibitor concentrations except in the case of CF_3H where solutions converged only for values of CF_3H mole fraction less than about 0.05. The numerical calculations predict burning rate reductions within the experimental uncertainty of the experimental results for CH_2F_2 and CF_4; the calculations for CF_3H show about 35% more reduction in the burning rate than the experiments. In all cases, the numerical calculations which assume the inhibitors to be inert show less inhibition than is observed in the experiments, and the calculations which allow full chemistry provide closer agreement with the experimental results.

Even at this early stage of development, the NIST fluorine-inhibition mechanism predicts the burning rate reduction quite well for these flames. The experiments and the modeling results indicate that CF_4, CF_3H, and CF_2H_2 all work somewhat better than if they act as inert species. The inhibition index suggested by Fristrom and Sawyer[17] is 1.5 to 2.0 for the fluorinated agents. For comparison, this index is 16.0 for CF_3Br[18] and 0.86 for CO_2[4]. Future research will continue mechanism refinement and validation and examine the chemical kinetic mechanisms of inhibition of hydrocarbon flames by fluorinated species.

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Figure Captions:

Figure 1 - Average burning rate determined using the total area method from the schlieren image of the premixed methane-air flame in the nozzle burner as a function of fuel-air equivalence ratio, together with the experimental results of Law *et al.* and Rosser *et al.* The solid is the calculated burning rate.

Figures 2 to 4 - Burning rate of premixed methane-air flame normalized by the uninhibited burning rate as a function of the inhibitor mole fraction for CF_4, CF_2H_2, and CF_3H at fuel-air equivalence ratios of 0.9, 1.00, and 1.1. The symbols present the experimental data and the lines the results of the numerical calculation. The numerical results are shown for calculations in which inhibitor reaction is permitted (solid lines) and in which the inhibitor is present but non-reacting (dotted lines).

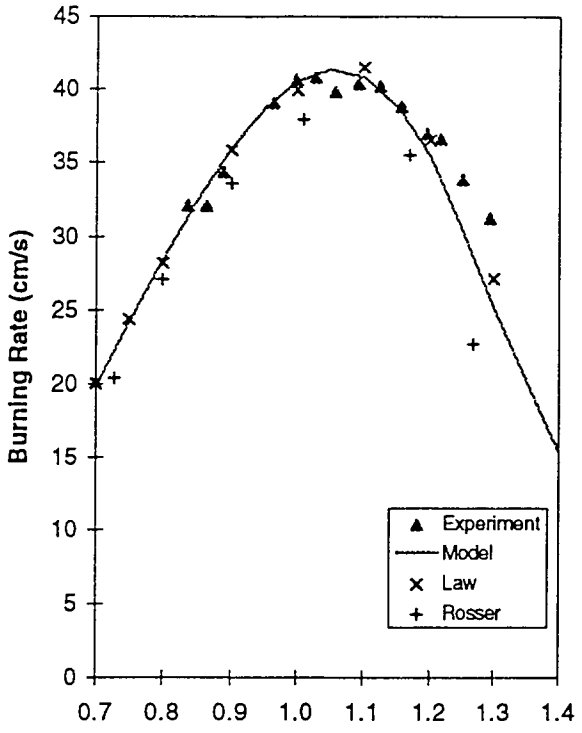

Figure 1

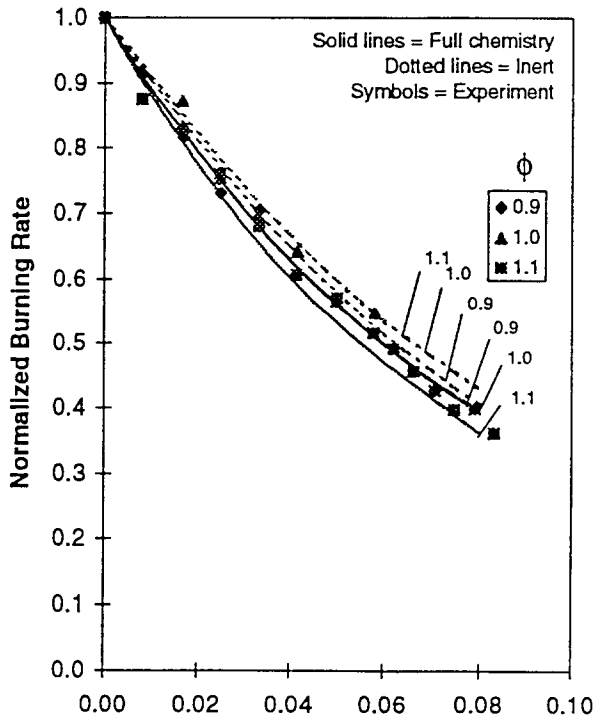

Figure 2

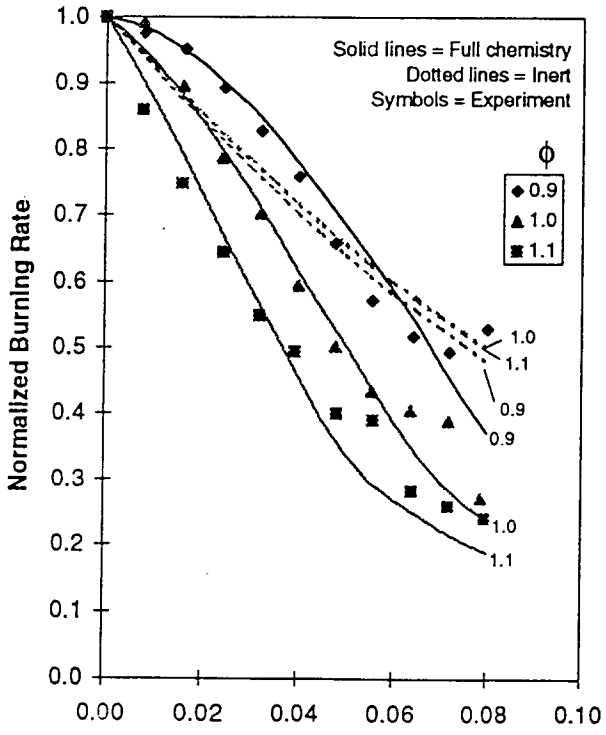

Figure 3

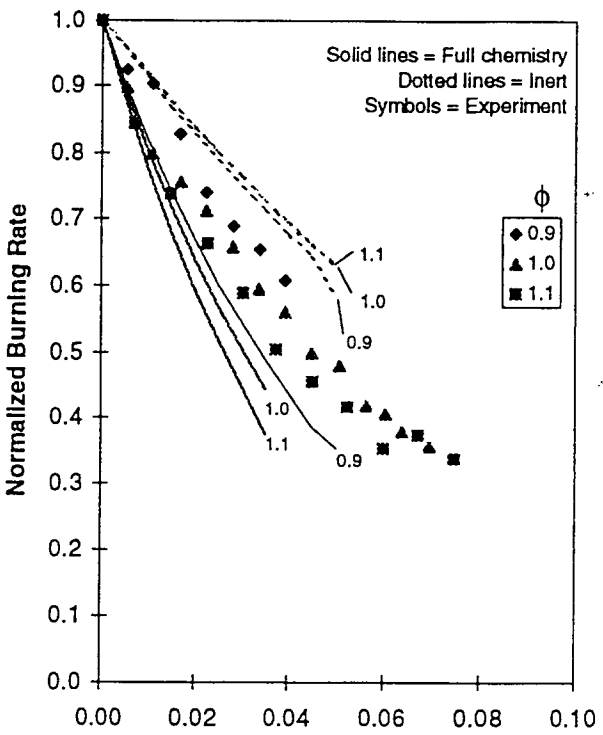

Figure 4