BURNING RATE OF PREMIXED METHANE-AIR FLAMES INHIBITED BY FLUORINATED HYDROCARBONS

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Introduction: The agents which are currently being considered as replacements for fire suppressant agent CF₂Br are mostly fluorinated hydrocarbons and perfluorinated alkanes. This abstract describes measurements of the reduction in burning rate of premixed methane-air flames with the addition of the single carbon inhibitors CF₄, CF₃H, CF₂H₂, and CF₃I. Early studies of the inhibitory effects 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. Premixed flame burners have flow fields which are relatively easily characterized, making interpretation of the inhibitor's effect on the overall reaction rate straightforward.

Experiment: In the present research, the flame speed measurements are performed using a nozzle burner. The burner consists of a quartz tube 27 ± 0.1 cm long with an area contraction ratio of 4.7 ± 0.1 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. 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%. A frame-grabber board in an Intel 486-based computer digitizes the image from a 512 by 512 pixel CCD array for subsequent analysis, and the mass burning rate is determined using the total area method. The product gas temperature 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 μm) allow correction for radiation losses.

Model: The structure of the inhibited premixed methane-air flame is calculated for CF₄, CF₃H, and CF₂H₂ using currently available techniques. The equations of species and energy conservation are solved numerically for the initial gas compositions of the experiments. The calculations employ a chemical kinetic mechanism recently developed at NIST which uses Miller and Bowman hydrocarbon sub-mechanism (140 reactions) and adds C₁ (200 reactions) and C₂ (400 reactions) fluorochemistry. Fluorinated-species reaction rates and thermochemical data are from the literature when available and are otherwise estimated.

*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.
Results and Discussion: The measured burning rate of the uninhibited methane-air flame as a function of equivalence ratio is in good agreement with previously published results\textsuperscript{2,12} and with the prediction of the numerical model. The reduction in burning rate is determined for the fluorinated inhibitors CF\textsubscript{4}, CF\textsubscript{3}H, CF\textsubscript{2}H\textsubscript{2}, and CF\textsubscript{3}I in near-stoichiometric premixed methane-air flames at inhibitor concentrations up to about 4\%. 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\textsubscript{4}, CF\textsubscript{3}H, and CF\textsubscript{2}H\textsubscript{2} all work somewhat better than if they act as inert. The agent CF\textsubscript{3}I reduces the burning rate about six times greater than the fluorinated agents. The inhibition index suggested by Fristrom and Sawyer\textsuperscript{13} is 1.5 to 2.0 for the fluorinated agents and 11.0 for CF\textsubscript{3}I. For comparison, this index is 16.0 for CF\textsubscript{3}Br\textsuperscript{14} and 0.86 for CO\textsubscript{2}\textsuperscript{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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