

Suppression of Nonpremixed Flames by Fluorinated Ethanes and Propanes

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Suppression of methane/air and propane/air nonpremixed counterflow flames, and n-heptane and methanol cup burner flames by fluorinated hydrocarbons was investigated. Four fluorinated ethanes, 10 fluorinated propanes, four bromine- or iodine-containing halons, and the inert agents CF_4 , SF_6 , and N_2 were tested in some or all of the flames. Laser Doppler velocimetry (LDV) determinations of peak velocity gradients in the oxidizer flow of the counterflow flames were found to be linearly correlated with the expression for global strain rate derived for plug flow boundary conditions. This correlation was used to estimate strain rate values at extinction. The bromine- or iodine-containing agents are more effective on a molar basis than the fluorinated propanes, followed by the fluorinated ethanes, and finally SF_6 , CF_4 , and N_2 . Agent effectiveness increases with the number of CF_3 groups present in the agent molecular structure. Numerical investigations of the flame speed reduction of methane/air mixtures doped with either CHF_2CHF_2 or $\text{CF}_3\text{CH}_2\text{F}$ predict that the latter is the better agent, in accord with experimental observations. Chemical contributions to suppression account for less than 35% of the total suppression offered by fluorinated hydrocarbons not containing bromine or iodine. At strain rates below 100 s^{-1} , suppression effectiveness rankings in methane and propane counterflow flames are similar to those obtained in n-heptane and methanol cup burner flames. Methanol flames are more difficult to extinguish than the alkane flames investigated, particularly with the chemical agent CF_3Br . © 2000 by The Combustion Institute

INTRODUCTION

The need for environmentally acceptable substitutes for bromine-containing halons (halogenated hydrocarbons) has led to a number of studies on alternative fire suppression agents encompassing a variety of experimental geometries and scales [1, 2], as well as to the development of chemical kinetic models for these agents [3–5]. Models are instrumental in guiding the search for effective halon replacements in that they facilitate the identification of mechanisms key to suppression. Such models must be validated using experimental data. Data sets that can directly be compared to numerical results are therefore particularly valuable. For models of suppression in particular, the usefulness of experimental and numerical studies depends on how well they capture the characteristics of real fire scenarios. Most experimental

studies on hydrofluorocarbons (HFCs), used as near-term halon replacements, have focused on inhibited premixed flames, usually with methane fuel, measuring parameters such as flame speed [6, 7] or profiles of intermediate species [8–10]. However, most fire-fighting scenarios involve higher hydrocarbon fuels, nonpremixed flames, and aim to achieve extinction rather than inhibition. In order to extend laboratory results to more realistic situations, a broad range of data sets is needed to provide adequate model validation for suppression by both HFCs and other classes of alternative agents now being identified.

The study described in the present paper focuses on the suppression effectiveness of HFCs in extinguishing nonpremixed flames. Although less effective fire suppressants than brominated halons, these agents are currently used as near-term replacements. They possess many of the same favorable physical properties as brominated halons, but do not destroy the stratospheric ozone layer [2, 11]. Previously, our laboratory investigated nonpremixed counterflow methane/air and propane/air flames suppressed by CF_4 , CHF_3 , and CF_3Br [12]. Here,

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TABLE 1
Agents Tested

Agent	Chemical Formula	C_p^{300K} (J/mol.K) ^a	$H^{1600K}-H^{300K}$ (kJ/mol) ^b	Flames ^c
HFC-134	CHF ₂ CHF ₂	90.9	183 ^[31]	M,P,H
HFC-134a	CF ₃ CH ₂ F	87.2	186 ^[31]	M,P,H
HFC-125	CF ₃ CHF ₂	95.9	195 ^[31]	M,P,H
FC-116	CF ₃ CF ₃	107.7	206 ^[31]	M,P,H
HFC-245ca	CHF ₂ CF ₂ CH ₂ F	123.7	244 ^c	M,P
HFC-245cb	CF ₃ CF ₂ CH ₃	123.0	242 ^c	M,P
HFC-245eb	CF ₃ CHFCH ₂ F	123.0 ^c	242 ^c	M
HFC-245fa	CF ₃ CH ₂ CHF ₂	122.0 ^[35]	241 ^[35]	M
HFC-236cb	CF ₃ CF ₂ CH ₂ F	130.0 ^c	256 ^c	M,P,H
HFC-236ea	CF ₃ CHFCHF ₂	129.8	256 ^c	M,P,H,A
HFC-236fa	CF ₃ CH ₂ CF ₃	128.1	253 ^c	M,P,H,A
HFC-227ca	CF ₃ CF ₂ CHF ₂	140.0 ^c	276 ^c	M,P,H
HFC-227ea	CF ₃ CHFCF ₃	139.8	275 ^[38]	M,P,H,A
FC-218	CF ₃ CF ₂ CF ₃	150.6	289 ^c	M,P,H
Halon 1301	CF ₃ Br	70.5	125 ^[36]	P,H,A
Halon 13001	CF ₃ I	61.3 ^[36]	126 ^[36]	P,H
Halon 1211	CF ₂ ClBr	74.6 ^d	133 ^[39]	P,H
Halon 1201	CHF ₂ Br	58.7 ^d	120 ^[39]	P,H
Sulfur hexafluoride	SF ₆	97.4 ^[36]	185 ^[36]	M,P,H
Tetrafluoromethane	CF ₄	61.2	122 ^[36]	H,A
Nitrogen	N ₂	29.1 ^[36]	42 ^[36]	M,P,H,A

^a Specific heat at 300 K. The numerical superscripts in square brackets indicate reference numbers. If no superscript is present, the value is from [34].

^b Sensible enthalpy required to raise the agent's temperature from 300 K to 1600 K. The sources for the data used to derive the sensible enthalpy values are indicated by the numerical superscripts in square brackets.

^c Estimated.

^d From [37], evaluated at 298 K.

^e Flames in which given agent was tested: M, methane counterflow; P, propane counterflow; H, n-heptane cup burner; A, methanol cup burner.

we extend the methane/air and propane/air extinction studies to include all fluorinated ethanes containing at least four fluorine atoms, and 10 fluorinated propanes containing at least five fluorine atoms. The fluorinated ethane and fluorinated propane data sets were generated to provide additional input to validate chemical kinetic models such as those developed recently for HFCs [3, 4, 5, 8]. Also tested in the present study were sulfur hexafluoride (SF₆, largely inert [13]), nitrogen, three bromine-containing halons, and one iodine-containing halon. All compounds investigated are listed in Table 1.

An experimental geometry that captures many characteristics of pool fire threats is that of the cup burner. Bench scale coflow burners operated with a liquid fuel, cup burners are widely used for estimating agent concentrations required to combat fires [14]. Hamins et al. [11] compared a number of HFC agents in cup

burner tests using five different fuels: n-heptane, two types of jet fuel, and two types of hydraulic fluid. For nearly all agents tested, the concentrations required to extinguish the n-heptane flame exceeded those required for the other fuels by less than 10%. Thus, n-heptane cup burner studies provide extinction data applicable to many fires.

For validation of kinetic models, treating detailed chemical mechanisms in the two-dimensional model required to describe cup burner flames is computationally difficult. An alternative to cup burners for suppression mechanism studies is provided by nonpremixed counterflow flames. This configuration is computationally tractable since it can be modeled quasi-one-dimensionally, along the axis of symmetry of the flame, by invoking a similarity transform [15]. Experimentally, it is also advantageous in that it allows control of the strain

rate imposed on the flame. In this paper, the strain rate in a counterflow burner is defined as the maximum axial gradient in axial velocity on the oxidizer side of the flame zone. The strain rate is easily adjusted by changing the gas flow rates. The effects of suppression agents can then be quantified over a range of flame conditions by measuring the extinction strain rate as a function of agent concentration. Hamins et al. [11] and Saso et al. [16] found that HFC extinction concentrations for low strain rate n-heptane counterflow flames were similar to those obtained in n-heptane cup burners. Since the cup burner configuration is relevant to many fire scenarios, the results of Hamins et al. and Saso et al. suggest that agent extinction concentrations in low strain rate nonpremixed counterflow flames are pertinent to these same scenarios.

The choice of a model fuel compound for suppression studies involves a trade-off between representative extinction properties and computational tractability. Gaseous fuels including methane, ethane, and propane are attractive to use from both experimental and modeling standpoints, but their relevance to fires involving long chain hydrocarbons needs to be determined. Furthermore, no model fuel is representative of all fire threats. Indeed, alcohol fires, methanol fires in particular, are very difficult to extinguish, even with CF_3Br [17]. The extinction behavior of methane/air counterflow, propane/air counterflow, n-heptane cup burner, and methanol cup burner flames are compared in this study to identify systematic trends in the suppression effectiveness of selected agents as a function of the fuel used. In addition to providing experimental data for HFC model validation, another objective of the current investigation is to assess whether methane or propane counterflow burner extinction studies are appropriate models for HFC suppression of liquid hydrocarbon fires.

Tanoff et al. [18] recently computed the extinction strain rate of methane/air counterflow flames suppressed by several C_1 and C_2 HFCs. One of their major conclusions was that most HFCs investigated, with the exception of CHF_3 , would be better suppressants in methane flames if they were chemically inert. Also, agents predicted to form CF_2O in the counterflow flame, principally from CF_3 radicals, were found to be

better suppressants than those that do not. The chemical contribution to suppression of the CF_3 group was reported by Sheinson et al. [13], who attributed 25% of CF_3Br 's suppression ability to this moiety. The present study further investigates the impact of CF_3 groups in an agent on suppression by comparing the performance of four sets of HFC isomers.

In counterflow burners, flow rates at extinction are apparatus-dependent. Comparisons between results obtained from different experimental and numerical counterflow flame studies must therefore be made through extinction strain rates. While flow rates are easily determined, velocity profile measurements are required to determine local extinction strain rates. In the present study, a burner-specific relationship between local strain rate and flow conditions is obtained. All strain rates quoted herein are therefore traceable to an experimental determination of the local velocity field.

EXPERIMENT

The counterflow burner and experimental methodology have been described previously [12]. The burner consisted of two vertically mounted open straight tubes, approximately 50 cm long, having an inner diameter of 1 cm. The tube exits were spaced 10.0 ± 0.5 mm apart. The gap size was determined by translating the burner assembly with respect to a laser beam perpendicular to the tube axis, and measuring the height at which the beam was blocked by the tubes. Each tube was surrounded by a co-annular tube having an outer diameter of 1.8 cm. Coflows through these tubes were not used in the present study as they did not measurably affect flame stability or extinction strain rate values. The top tube was equipped with a cooling jacket to prevent the hot combustion products from preheating the upper reactant stream. The tubes were housed in a Plexiglas chamber, which was continuously purged with nitrogen to dilute combustion products and unburned reactants before they entered the exhaust.

For experiments with methane, the fuel was introduced through the top tube while air/agent mixtures were introduced through the bottom. For experiments with propane, air/agent mix-

tures were delivered from the top, fuel from the bottom. These configurations were used because they produced the most stable flames at low strain rates. For propane, inverting the reactant streams did not significantly affect the extinction strain rate of the uninhibited flame. Flow rates of all gases were regulated by mass flow controllers (Sierra Instruments, Monterey, CA, USA), which were calibrated using a piston flowmeter (DC-2, Bios International, Pompton Plains, NJ, USA). All flow conditions used in the present study were laminar, with tube Reynold numbers never exceeding 2100.

During extinction measurements, the flow rates of fuel and air were set to obtain a flame midway between the tubes. The agent flow was then slowly increased at intervals of 30–45 seconds, with periodic adjustments of the fuel and air flows to maintain the flame's position, until the flame extinguished. The flame's position was determined by monitoring its image on a video screen. The stagnation plane was always slightly toward the fuel tube from the flame zone. In experiments with methane, the flame typically extinguished completely. For propane, local extinction typically occurred along the centerline, leaving a ring-shaped flame with a hole along the burner axis, similar to that described by Potter and Butler [19]. In all tests, the agent was added to the air stream. This mode of application most closely resembles actual situations, in which an agent is introduced into the air around the fire, with the fuel burning in a nonpremixed flame.

The cup burner apparatus and methodology have been described in detail elsewhere [13]. The design was virtually identical to that of Hamins et al. [11]. The piston flowmeter was used to measure the agent and air flows after each extinction measurement. The total flow rate of air + agent was 20 ± 1 liters/minute for all extinction measurements, giving a flow velocity, averaged over the 105 mm inner diameter chimney, of 4.1 ± 0.2 cm/s past the 28 mm outer diameter cup. Experiments were conducted on both n-heptane and methanol flames. The fuel level was kept within 0.5 mm of the top of the cup without overflowing, as low liquid levels led to attachment of the flame to the heated rim of the Pyrex cup, resulting in anomalously high extinction values.

The n-heptane used in the cup burner experiments was 97.5% pure, from Burdick & Jack-

son, Muskegon, MI. The A.C.S. grade methanol was 99.9% pure, from Fisher Scientific, Muskegon, MI. The air used in both cup and counterflow burners was either from the Naval Research Laboratory's in-house supply of compressed breathing air cylinders, or from a building supply line. The building air was filtered to remove any particulates and aerosols from the air supply stream.

The agents listed in Table 1 were obtained from the following suppliers: HFC-245eb and Halon 13001, Flura, Rock Hill, TN; HFC-245fa, AlliedSignal, Morristown, NJ; HFC-236ea and HFC-236fa, DuPont, West Lafayette, IN; HFC-227ea and Halon 1201, Great Lakes Chemical; FC-218, Scott Specialty Gases, Plumsteadville, PA; Halon 1301 and CF_4 , Matheson (Parsippany, NJ). The nitrogen was obtained from the Naval Research Laboratory's in-house supply. The remaining agents were from PCR (Gainesville, FL). The stated purity of the agents was at least 97%. All agents were used as supplied, with the exception of HFC-245ca, HFC-245eb, and HFC-245fa. These pentafluoropropanes have boiling points close to room temperature: 25°C, 23°C, and 15°C respectively. They were therefore premixed with air in a 1:3 ratio before being tested. The pressure increase ensured that stable flows of these agents were delivered to the burners. Extinction data was also collected with HFC-245fa unmixed with air. This data was consistent with that obtained using the agent/air mixture.

All agents investigated in the present study were tested in the propane counterflow flame with the exception of HFC-245eb, HFC-245fa, and CF_4 , as shown in Table 1. All of the agents were tested in the methane counterflow flame with the exception of Halon 1301, Halon 13001, Halon 1211, Halon 1201, and CF_4 . All of the agents with the exception of the pentafluoropropanes were tested with n-heptane in the cup burner. HFC-236ea, HFC-236fa, HFC-227ea, Halon 1301, CF_4 , and nitrogen were tested with methanol in the cup burner.

EXTINCTION STRAIN RATE DETERMINATION

Many researchers performing studies in counterflow burners have characterized extinction

conditions in terms of global or imposed parameters, such as flow rates and gap size [20], or global strain rates calculated from these parameters [11, 21]. These global parameters representing the imposed flow conditions can be compared to the same parameters obtained from numerical calculations of extinction conditions [22]. Because the local flow field near the flame determines extinction, the comparison of global parameters is valid only as long as the relationship between the local strain rate and the global conditions are the same for the experiment and the calculations. Recent measurements [15, 23] have cast doubts on the adequacy of representing counterflow experimental boundary conditions by either plug or potential flow in numerical calculations. Comparisons of measured and numerical local strain rates in the vicinity of the flame should show less sensitivity to boundary conditions than comparisons of measured and numerical global strain rates.

The most direct approach in determining strain rate is to measure the local velocity fields. As velocities can not be measured at extinction, determination of local extinction strain rate involves a series of velocity measurements in increasingly strained flames, and extrapolation to extinction [12]. This sequence of measurements must be repeated for each fuel/oxidizer/additive system and each additive loading, requiring large numbers of velocity profile measurements.

In the present study, air stream local strain rates were determined by measuring the center-line axial velocity as a function of axial position by an LDV system (QSP Digital, Irvine, CA). The oxidizer stream was seeded with 0.3-micron alumina particles (Buehler, Lake Bluff, IL). The velocity profile on the oxidizer side of the flame was fit to a 6th-order polynomial, and the relevant local strain rate was taken to be the maximum value of the derivative of this function. Velocity profiles were measured for propane/air, methane/air, methane/(air + HFC-227ea), and propane/(air + SF₆) flames.

Based on these measurements, an empirical, burner-specific relationship to convert global parameters into local strain rates was determined. Figure 1 shows the data used in obtaining this correlation. Measured local strain rate is plotted versus the plug flow global strain rate

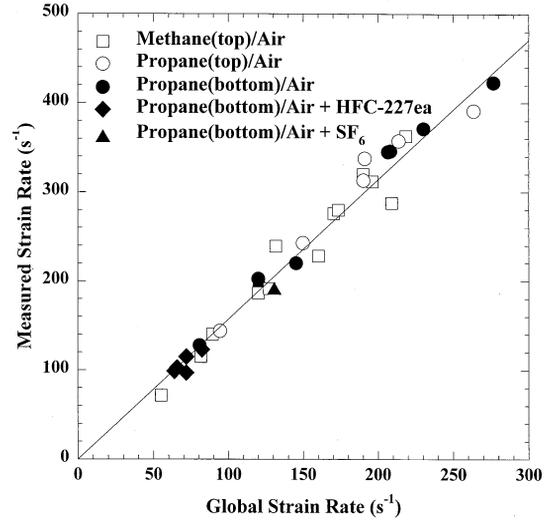


Fig. 1. Comparison of local strain rates measured by LDV in nonpremixed counterflow flames and global strain rates calculated from Eq. 1. The solid line corresponds to the linear regression given in Eq. 2.

parameter derived by Seshadri and Williams [24], and restated by Chelliah et al. [15]:

$$K_{\text{global, plug}} = \frac{2|V_o|}{L} \left(1 + \left(\frac{\rho_f V_f^2}{\rho_o V_o^2} \right)^{0.5} \right), \quad (1)$$

where L ($= 1$ cm) is the gap size, and $\rho_{f,o}$ and $V_{f,o}$ are the densities and velocities of the fuel and oxidizer streams, respectively. V is taken as the *average* velocity across the tube exit. Measured local strain rates for all flame conditions, including those with suppressants present, were proportional to $K_{\text{global, plug}}$ from Eq. 1,

$$K_{\text{local}} = (1.57 \pm 0.02) K_{\text{global, plug}}, \quad (2)$$

where the velocities used in the global expression are averages based on measured volumetric flow rates. The local extinction strain rates discussed in the present study were obtained using Eqs. 1 and 2.

Seshadri and Williams' plug flow global strain rate expression is for the axial gradient in axial velocity at the stagnation plane calculated for inviscid nonreacting flow, with plug flow boundary conditions imposed at the burner exits. The current apparatus, with straight burner tubes, has velocity boundary conditions significantly different from plug flow. Measurements near the tube exits indicate a nearly parabolic profile for an individual tube in isolation, with some

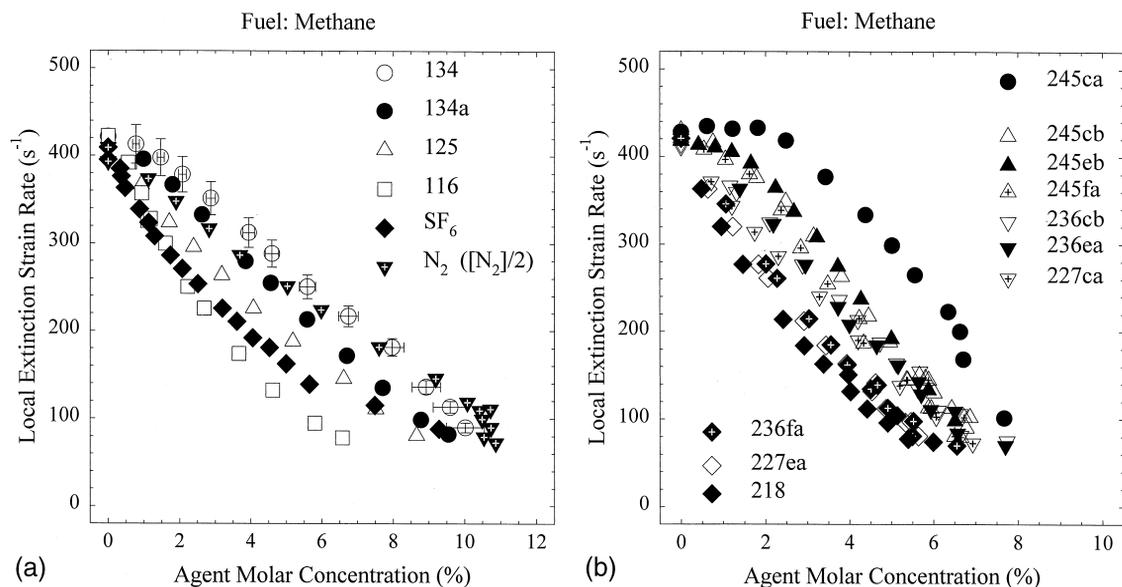


Fig. 2. Extinction strain rate versus agent molar concentration for nonpremixed methane/air flames suppressed by: (a) fluorinated ethanes, SF₆, and N₂; and (b) fluorinated propanes. The error bars shown for the HFC-134 data at the 99.7% (3 σ) confidence level are typical of all data sets shown in Fig. 2.

flattening of the profile when the opposing flow from the second tube is introduced. The center-line velocity of a parabolic profile in tube flow is twice the average velocity determined from the volumetric flow rate and the cross-sectional area. At a given flow rate, the tube exit center-line velocities in the current apparatus are therefore expected to be between once and twice the plug flow values. Hence, the coefficient relating K_{local} and $K_{\text{global,plug}}$ is predicted to lie between 1 and 2. The factor of 1.57 obtained is consistent with this prediction. Pellett et al. [25] also determined that local and global strain rates were linearly related in their opposed-tube burners: local strain rates were found to be 3 times larger than their global counterparts. Pellett et al. used burners with a ratio of gap size to tube diameter equal to 2. For the burner considered in the present study, this ratio is equal to 1.

NONPREMIXED COUNTERFLOW FLAME EXPERIMENTS

Figures 2 and 3 show how local extinction strain rate varies with agent molar concentration, for methane and propane nonpremixed counterflow flames respectively. Figures 2a and 3a show

the suppression effects of the fluorinated ethanes, SF₆ and N₂. The N₂ extinction concentrations have been divided by 2 for presentation in the figures. Figures 2b and 3b show results for the fluorinated propanes. Figure 3c shows the effects of Halon 1301, Halon 13001, Halon 1211, and Halon 1201 on the extinction strain rate of a propane flame. The error bars shown in Figs. 2a and 3a for the HFC-134 data are at the 99.7% (3 σ) confidence level. Horizontal error bars represent uncertainties in air and agent flow rates. Vertical error bars represent uncertainties in air, agent and fuel flow rates, gap size, room temperature and pressure, and the constant of proportionality between local and global strain rates (Eq. 2). At comparable concentrations or extinction strain rates, uncertainties in the data for the other agents are similar to those shown for HFC-134. The N₂ extinction concentration uncertainties are similar to those for HFC-134 at comparable loadings. They increase to ± 1.7 mole % at the highest concentrations.

Extinction of Uninhibited Methane and Propane Flames

The uninhibited flame local extinction strain rates for methane and propane were found to

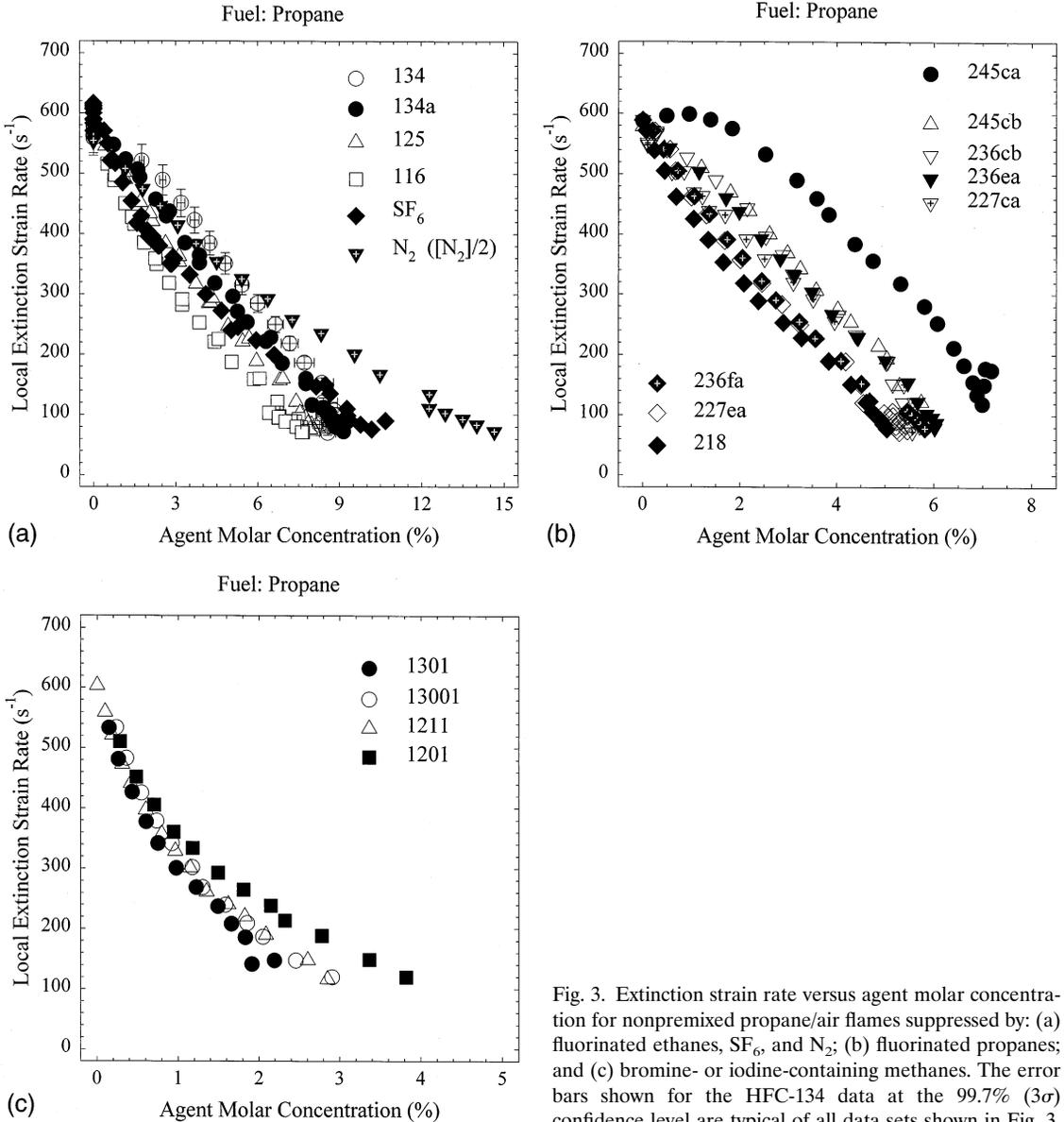


Fig. 3. Extinction strain rate versus agent molar concentration for nonpremixed propane/air flames suppressed by: (a) fluorinated ethanes, SF₆, and N₂; (b) fluorinated propanes; and (c) bromine- or iodine-containing methanes. The error bars shown for the HFC-134 data at the 99.7% (3σ) confidence level are typical of all data sets shown in Fig. 3.

be $415 \pm 32 \text{ s}^{-1}$ and $583 \pm 53 \text{ s}^{-1}$ (3σ level) respectively. Individual measurements are shown in Figs. 2 and 3. Uncertainties pertaining to the oxygen concentration in the air used to conduct the counterflow studies are not accounted for in the strain rate error bars. Based on the N₂ results of Figs. 2a and 3a, K_{local} 's sensitivity to the air's oxygen content is estimated to be on the order of 75 and 110 s⁻¹ per mole % for uninhibited methane and propane flames respectively. The scatter in the measurements collected in the present investigation

indicates that oxygen mole fractions could not have varied by more than 0.5 mole %.

The average uninhibited nonpremixed counterflow methane/air and propane/air flame local extinction strain rates can be compared to values found in the literature. Pellett et al. [25] used two different opposed-nozzle burners to obtain extinction strain rates of 384 s⁻¹ and 396 s⁻¹ for methane/air flames. Furthermore, Chelliah et al. [15] measured the local extinction strain rate of their nonpremixed counterflow methane/air flame to be 380 s⁻¹. Yang and

Kennedy [26] measured theirs to be 340 s^{-1} . Both of these values were obtained for flames having strain rates below that required for extinction. They correspond to lower bounds for the values that would be calculated from an extrapolation to extinction, and are consistent with the results of the present study. Yang and Kennedy indicate that the strain rate they report is approximately 10% lower than that which would be obtained through extrapolation; and that the uncertainty in their critical strain rate is approximately +10% and -5%.

Global extinction strain rates for uninhibited counterflow nonpremixed methane/air and propane/air flames have also been reported in the literature. MacDonald et al. [27] report a global extinction strain rate of 296 s^{-1} for methane. The corresponding global value obtained in the present study is 273 s^{-1} . Since the experimental geometries in both studies are similar, the values are expected to be comparable. MacDonald et al. indicate that variations of up to 80 s^{-1} were observed in their uninhibited global extinction strain rates, due to variations in their air's oxygen content. The global methane extinction number collected in the present study is thus consistent with theirs. Puri and Seshadri [28] also report global extinction values for their methane/air and propane/air counterflow flames. Puri and Seshadri's experimental geometry differs from that of the present study. The scaling factors between local and global strain rates in the two studies are thus likely to be different. Therefore, global strain rates from the two studies can not be directly compared.

Agent Suppression Effectiveness

Figures 2 and 3 show that, in general, the extinction strain rate of both methane and propane flames decreases as agent loading increases. Thus, the agents act to inhibit the flames. For HFC-245ca, however, the extinction strain rates at concentrations below 2% are higher than those for the uninhibited flames. At these loadings, this agent increases flame strength. Nevertheless, above 2%, extinction occurs at strain rates below the uninhibited values, and extinction strain rates decrease with increases in concentration: in larger quantities, HFC-245ca does act like a suppressant. The

extinction data presented in Figs. 2 and 3 is limited to strain rates above 70 s^{-1} . Below this value, considerable scatter was observed and, for several agents, extinction concentrations began to decrease with diminishing strain rate. At low strain rates, the flames become more susceptible to both conductive and radiative heat losses to the burner, and to fluctuations in the flow currents present in the surrounding chamber gases.

A secondary flame zone about 1 mm on the air side of the principal nonpremixed flame was observed in tests with HFC-245ca, particularly at high loadings. Hamins et al. [11] also found separate agent and fuel consumption zones in their numerical investigation of the structure of Halon 1301 inhibited n-heptane/air nonpremixed counterflow flames. In the current study, the secondary flame zone appears to be caused by the agent burning in the air in a premixed fashion. Yang et al. [29] predicted this phenomenon for CH_3Cl addition to the oxidizer stream of a methane/air counterflow flame. Although HFC-245ca is nonflammable at ambient temperature and pressure, heat release from the nonpremixed flame was apparently sufficient to support its premixed combustion. Grosshandler et al. [30] investigated the flammability of HFC-245ca, and concluded that a stoichiometric mixture of HFC-245ca and air could sustain combustion if preheated 100 K above ambient temperature. A secondary flame zone was also observed in tests with a more effective suppressant, HFC-245cb, but was less pronounced than in the HFC-245ca case.

The relative suppression effectiveness of the fluorinated propanes can be assessed from Figs. 2b and 3b. The most effective fluorinated propanes are FC-218, HFC-227ea, and HFC-236fa, all of which contain two CF_3 groups. HFC-227ca, HFC-236ea, HFC-236cb, and HFC-245cb, along with HFC-245fa and HFC-245eb in the methane case, are less effective and contain one CF_3 group. HFC-245ca has no CF_3 groups and is clearly less effective than the other fluorinated propanes tested. The extinction strain rate curves cluster together in terms of the number of CF_3 groups present in the agent.

Among agents with the same number of CF_3 groups, compounds with higher fluorine to hydrogen atom (F:H) ratios are slightly more

effective agents, particularly at low concentrations: FC-218 is slightly more effective than HFC-227ea and HFC-236fa; and HFC-227ca, HFC-236ea, and HFC-236cb are more effective than the pentafluoropropanes. At higher concentrations, agent suppression effectiveness is not as affected by the F:H ratio. The impact on suppression of substituting an F atom for an H atom in the agent molecule is both chemical and physical in nature. F atoms can scavenge H atoms in flames to form HF, reducing the number of H's that participate in flame propagation reactions [10]. Furthermore, as shown in Table 1, substituting one F for one H in a fluorinated propane leads to a 5 to 8% increase in its specific heat at 300 K, enhancing the molecule's sensible enthalpy. Higher F:H ratios are therefore expected to increase the physical suppression effectiveness of fluorinated propanes. However, as the data shows, the effect of substituting one H for an F is minor compared to that of arranging the fluorines to provide a CF_3 group: HFC-236fa is more effective than HFC-227ca, which has one more fluorine atom but one less CF_3 group.

The impact of CF_3 groups on suppression is further illustrated by the fluorinated ethane results shown in Figs. 2a and 3a. FC-116, which has two CF_3 groups, is more effective than HFC-125 and HFC-134a, which only have one. HFC-134, which contains no CF_3 groups, is the least effective of the fluorinated ethanes for most flame conditions. The presence of additional fluorine atoms in FC-116 and HFC-125 could explain their enhanced effectiveness relative to HFC-134a and HFC-134. However, the tetrafluoroethanes have the same number of fluorine atoms. At strain rates above 100 s^{-1} , HFC-134a is more effective than HFC-134, which correlates with the presence of a CF_3 group in the former. At lower strain rates, the extinction concentrations of these two agents are comparable.

The presence or absence of a CF_3 group also influences the suppression effectiveness of the halons shown in Fig. 3c. This figure shows that Halon 1201 (CHF_2Br) is less effective than both Halon 1301 (CF_3Br) and Halon 13001 (CF_3I), particularly at higher loadings; and Halon 1211 (CF_2ClBr) is observed to be slightly less effective than Halon 1301. Sheinson et al. [13] inves-

tigated the chemical suppression effectiveness of the CF_3Y and SF_5Y ($\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) series in an n-heptane cup burner. They concluded that, for CF_3Cl , the CF_3 moiety made a greater chemical contribution to suppression than the Cl atom. This conclusion is consistent with the greater effectiveness of Halon 1301 relative to Halon 1211 observed in the present study.

Fluorinated Ethanes Versus Fluorinated Propanes

The effectiveness of the fluorinated ethanes relative to that of the fluorinated propanes can be assessed by comparing Fig. 2a to Fig. 2b, and Fig. 3a to Fig. 3b. At strain rates below 100 s^{-1} , fluorinated ethanes are observed to extinguish methane flames at concentrations between 5 and 10%. Loadings between 4 and 8% are required for the fluorinated propanes. In the case of propane flames, below 100 s^{-1} , extinction concentrations for the fluorinated ethanes range from 6 to 10%. For the fluorinated propanes, they range from 4 to 8%. The steeper extinction strain rate curves for the fluorinated propanes indicate that, as a group, they are more effective agents on a molar basis than the fluorinated ethanes. Table 1 shows that the specific heats at 300 K of the fluorinated propanes range from 122.0 to $150.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, as opposed to 87.2 to $107.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for the fluorinated ethanes. The greater effectiveness of the fluorinated propane agents is consistent with their greater sensible enthalpy relative to the fluorinated ethanes.

Methane Flames Versus Propane Flames

Figures 2 and 3 can also be compared to assess the differences between suppression of methane and propane nonpremixed counterflow flames. The uninhibited propane flame is more difficult to extinguish, requiring an average strain rate of 583 s^{-1} versus 415 s^{-1} for methane. However, the extinction strain rates of flames fueled with propane decrease more rapidly with increases in suppressant loading such that, at strain rates below 100 s^{-1} , methane and propane flames are extinguished by similar fluorinated agent loadings. If the extinction strain rates are normalized by the corresponding uninhibited strain

rates and compared, the sensitivity of both methane and propane flames to agent addition is found to be similar. The propane flames are slightly more sensitive to the suppressants. Figs. 2 and 3 show that extinction strain rate curve shapes are different for the two fuels.

NUMERICAL INVESTIGATION OF TETRAFLUOROETHANE ISOMER EFFECTIVENESS

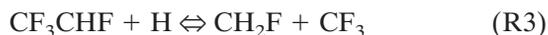
The kinetic model developed at the U.S. National Institute of Science and Technology (NIST) [31] for fluorinated hydrocarbons has been used to numerically investigate the effects of halogenated compounds on C_1 and C_2 organic flames [3, 7, 18, 32]. With this model, Tanoff et al. [18] predicted extinction strain rates for methane/air counterflow flames suppressed by CF_4 , CHF_3 , CF_3CF_3 (FC-116), CF_3CHF_2 (HFC-125), and CF_3CH_2F (HFC-134a). The NIST model was also used by Linteris et al. [7], who reported both experimental and computational flame speeds for methane/air mixtures containing FC-116, HFC-125, and HFC-134a. Reaction pathway analyses of agent decomposition showed that CF_2O was an important intermediate for FC-116, which initially decomposes to form two CF_3 radicals. The numerical calculations predict that as the hydrogen content of the fluorinated ethane increases, less CF_2O is produced. To our knowledge, no previous modeling studies have compared different isomers. In the present form of the kinetic mechanism, only fluoroethane isomers may be compared, because the fluorocarbon kinetic mechanism, in its original form, does not include C_3 species. Recently, the mechanism has been extended to cover HFC-227ea [4, 5, 33]. Kinetic mechanisms for other fluoropropanes have not yet been developed.

In the present study, calculations were conducted using the NIST model to predict flame speeds of stoichiometric methane/air mixtures doped with 3.81 mole % of either HFC-134 or HFC-134a. The goal of these calculations was to determine if the current kinetic model predicts isomeric differences between the two agents, and why these differences may exist. Although extinction strain rate predictions, such as those

performed by Tanoff et al., are more relevant to the measurements of Figs. 2a and 3a, they are computationally more demanding. It is generally acknowledged that flame speed is closely related to extinction strain rate [19]. The current calculations, which predict isomeric differences in suppression, should therefore carry over to nonpremixed flames.

The flame speed calculations were performed on a domain extending 25 cm from the flame into the cold reactants, and 60 cm into the hot products. The calculations used multicomponent viscosities, thermal diffusivities for H and H_2 , and windward differencing for the convective terms. The initial temperature of the reactants was set to 298.2 K. The ultimate solutions were obtained on meshes having 150 grid points.

The kinetic mechanism used was essentially that developed by NIST, modified according to L'Espérance et al. [10]. The reactions



were taken from Linteris et al. [7]. Furthermore, the reactions

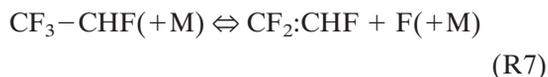


and



were also added. These latter two reactions are not present in the NIST mechanism, although the analogous reactions for all other pairs of fluorinated methyl radicals are included. The kinetic rates of reactions R5 and R6 were estimated by taking the geometric mean of the rates of the analogous reactions for $CH_3 + CF_3$ and $CHF_2 + CF_3$. R5 represents an additional destruction pathway for HFC-134a not considered in the modeling of Ref. 7.

Finally, the thermal decomposition reaction



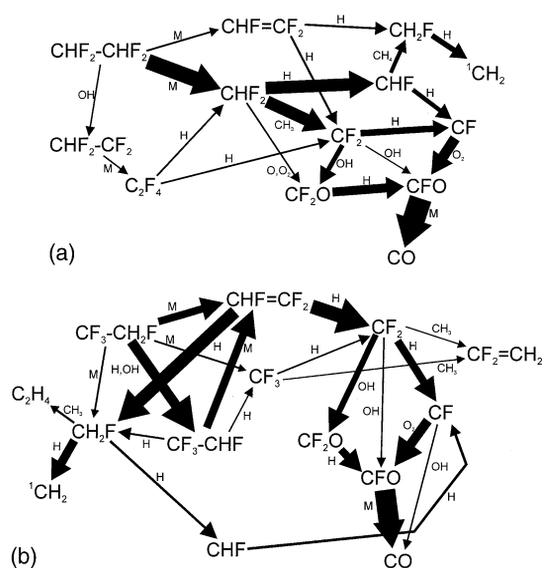


Fig. 4. Reaction pathways for premixed methane/air flames doped with 3.81 mole % of: (a) HFC-134; and (b) HFC-134a.

was added using the high-pressure kinetic expression from Ref. 5 and estimated low-pressure kinetics from Ref. 33. This reaction proved very important in modeling suppression by HFC-227ea, in which the $\text{CF}_3\text{-CHF}$ radical is formed from the parent agent by C–C bond dissociation. From HFC-134a, this radical is produced by hydrogen abstraction. The predicted flame speeds for the mixtures containing HFC-134 and HFC-134a were 18.9 cm/s and 15.5 cm/s, respectively, or 48% and 39% of the calculated uninhibited methane/air flame speed of 39.4 cm/s. For the HFC-134a case, the experimental measurement and numerical prediction of Linteris et al. [7] are 38% and 29%, respectively. Flame speed measurements for methane/air/HFC-134 mixtures have not been reported. Thus, the kinetic model does predict a substantial difference in inhibition effectiveness between the two tetrafluoroethane isomers. The refinements in the kinetic mechanism greatly improve agreement with the experimental flame speed measurement for HFC-134a. Reaction pathway diagrams for HFC-134 and HFC-134a are shown in Figs. 4a and 4b. The major removal pathway for $\text{CHF}_2\text{-CHF}_2$ is thermal dissociation of the C–C bond. For $\text{CH}_2\text{F-CF}_3$, the major removal pathways are hydrogen abstraction by H and OH, and HF elimination. Sensi-

tivity analysis indicates that these initial reaction steps have the greatest influence on the difference in flame speed between the two isomers. This may be a consequence of the major removal pathways for HFC-134a consuming H or OH and generating less reactive species, while the dominant HFC-134 pathway generates radicals. The reaction pathways associated with HFC-227ea should be representative of those of other fluorinated propanes. HFC-227ea, under most conditions, is consumed by thermal decomposition, not radical attack. The decomposition pathways are HF elimination and C–C bond removal. The latter process dominates in near-stoichiometric, high-temperature flames [33]. For asymmetric isomers, more than one product channel exists for most agent destruction reactions. If a fluorinated ethyl radical is produced by thermal decomposition, it is likely to decompose through H atom elimination from the methyl group, if one is present. Otherwise, F atom elimination will be the dominant process [33]. H and F are both reactive species. However, H has a higher diffusivity and participates in the $\text{H} + \text{O}_2$ chain-branching reaction, whereas F reacts primarily in a chain-propagating reaction with H_2O . These considerations provide one possible explanation for the observed isomeric differences among fluoropropanes. Kinetic mechanisms for these agents must be developed and validated before a more definitive analysis can be conducted.

CUP BURNER EXPERIMENTS

The n-heptane and methanol cup burner extinction concentrations obtained in the present study are provided in Table 2. Concentrations based on both volumetric and molar proportions are included. The two sets of values are not identical as several of the agents deviate from ideal gas behavior at ambient conditions. Each concentration represents the average of at least 3 runs. At the 99.7% confidence level (3σ), the uncertainties associated with the cup burner values are estimated to be ± 0.6 mole%, with the exception of those for CF_4 and N_2 , estimated to be ± 1.5 mole %. Table 2 also shows the n-heptane cup burner data (vol.%) of Hamins et al. [11]. Extinction concentrations

TABLE 2
Cup Burner Extinction Concentrations

Agent	n-Heptane Cup Burner (Present Study)		n-Heptane Cup Burner (Reference [11])	Methanol Cup Burner (Present Study)	
	Vol. %	Mol. %		Vol. %	Mol. %
Halon 1301	3.1 ^a	3.1	3.0	6.3	6.4
Halon 13001	3.2 ^a	3.2			
Halon 1211	3.6	3.7			
Halon 1201	4.1	4.1			
FC-218	6.1 ^b	6.3	6.4		
HFC-236fa	6.1	6.3	6.8	8.0	8.2
HFC-227ea	6.4	6.6	6.3	8.9	9.2
HFC-227ca	6.9	7.1			
HFC-236ea	7.2	7.5		9.9	10.3
HFC-236cb	7.4	7.7			
FC-116	7.9 ^a	8.0	8.4		
HFC-125	8.8	8.9	8.8		
HFC-134a	10.0	10.2	10.2		
Sulfur hexafluoride	10.6	10.9			
HFC-134	10.9	11.1			
Tetrafluoromethane	16.0 ^a	16.0		22.0	22.1
Nitrogen	30.0 ^a	30.0	31.8	41.6	41.6

^a From [13].

^b From [13], but corrected for typographical error.

from the two data sets are within 7% of each other for all agents except HFC-236fa, for which they differ by 11.5%.

Hamins et al. [11] and Saso et al. [16] compared cup burner values to extinction data collected in liquid n-heptane counterflow flames. Both studies found that counterflow extinction concentrations at low strain rates are similar to those obtained in a cup burner. To assess the impact of fuel type on extinction loadings, methane and propane counterflow values at low strain rates are compared in the present study to n-heptane and methanol cup burner values. An appropriate counterflow extinction strain rate must be selected to make the comparison. Hamins et al. used a global strain rate of 50 s^{-1} . Saso et al. used a global strain rate of 30 s^{-1} , but defined their global strain rate as one-half that used by Hamins et al. In this investigation, a local strain rate of 80 s^{-1} is chosen.

Figures 5a–5d show n-heptane cup burner, methanol cup burner, methane counterflow, and propane counterflow extinction results, respectively. For each fuel, the agents are presented in decreasing order of effectiveness, with

the most effective agent listed at the top of the bar chart. The methane and propane counterflow extinction values for N_2 are divided by 2 for presentation in the figure. The counterflow extinction concentrations for agents not tested at strain rates as low as 80 s^{-1} were extrapolated from the curves of Figs. 2 and 3.

Physical Versus Chemical Contributions to Suppression

Physical versus chemical contributions to suppression for different agents are compared following the formalism of Tucker et al. [17] and Sheinson et al. [13]. Physical contributions attributed to agent addition include increased thermal mass, oxygen dilution, and increased conductive heat losses for agents with high thermal conductivities such as helium. Sheinson et al. found that the dominant physical effect of most fluorinated agents is to add thermal mass. CF_4 and SF_6 , essentially inert, both extinguish n-heptane cup burner flames when the amount of agent added is such that the energy required to raise the temperature of the nitrogen and agent present, from 300 K to 1600 K, exceeds a

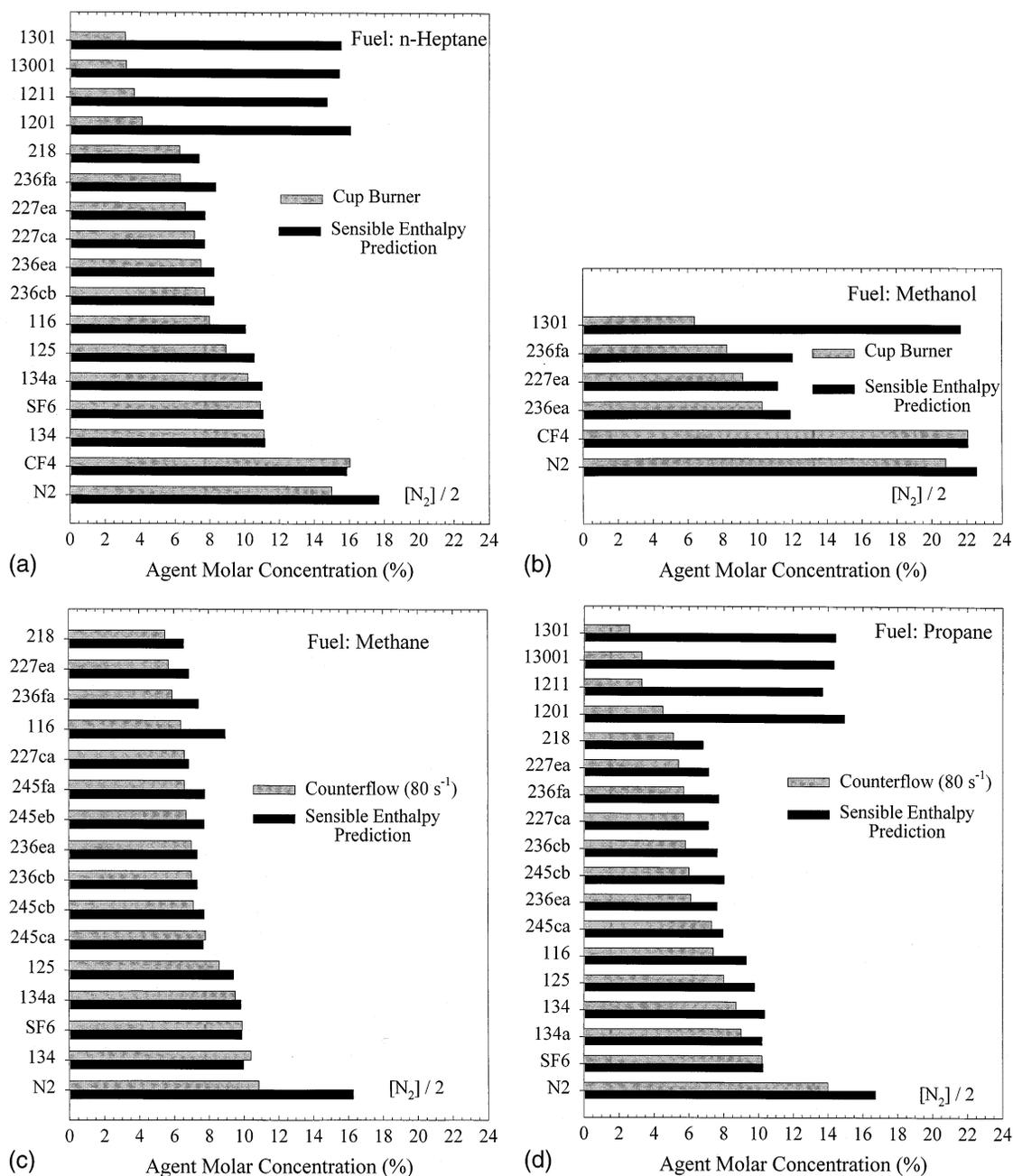


Fig. 5. Extinction concentrations for agents suppressing: (a) n-heptane/air cup burner flames; (b) methanol/air cup burner flames; (c) methane/air counterflow flames at a strain rate of 80 s^{-1} ; and (d) propane/air counterflow flames at a strain rate of 80 s^{-1} . The predicted agent extinction concentrations represent the loadings that would be required to suppress the given flames assuming that the agents were inert, and that they extinguished the flames at the same sensible enthalpy per mole of oxygen as CF_4 and SF_6 .

critical value. This critical value is proportional to the amount of oxygen supplied, and is similar for CF_4 and SF_6 . It is lower for nonfluorinated agents such as Ar, He, N_2 , and CO_2 , due to

greater contributions of thermal conductivity and oxygen dilution to suppression for these agents.

In the present study, the extinction concen-

tration for CF_4 was used to estimate the sensible enthalpy per mole of oxygen required to extinguish a methanol flame. The estimated extinction sensible enthalpy for this flame was found to be 322 kJ/mol O_2 . Similarly, SF_6 extinction concentrations were used to obtain extinction sensible enthalpies for methane and propane flames of 254 and 258 kJ/mol O_2 respectively. In the case of n-heptane, both CF_4 and SF_6 extinction concentrations were available. The SF_6 data led to a sensible enthalpy value 1% lower than that estimated from the CF_4 data. The average of the two values, 267 kJ/mol O_2 , was chosen as the extinction sensible enthalpy for the n-heptane flame.

Physical contributions to suppression of other compounds can be estimated by assuming that they are inert and that they extinguish a given flame at the same sensible enthalpy per mole of oxygen as CF_4 and SF_6 . The method is valid for compounds with physical contributions to suppression dominated by thermal mass addition, as they are for SF_6 and CF_4 . Physical predictions for the extinction concentrations of the agents tested in this study are shown in Fig. 5. The sensible enthalpies required to raise agent temperature from 300 K to 1600 K are provided in Table 1. A comparison of the measured and predicted extinction data reveals that the bromine- and iodine-containing compounds suppress flames mostly through chemical means, with physical contributions to suppression not exceeding 30% regardless of fuel type. For all of the other agents, the chemical contribution to suppression does not exceed 35%. The differences between the measured and predicted values for N_2 are consistent with the findings of Sheinson et al.. For HFC-134 and HFC-245ca in methane, the actual extinction concentrations are larger than the sensible enthalpy predictions. The net effect of fluorocarbon chemistry for these agents, which do not contain CF_3 groups, is to promote combustion.

Effect of Fuel Type on Suppression Effectiveness Ranking

The extinction data of Fig. 5 shows that agent effectiveness rankings are similar for the fuels tested. The bromine- or iodine-containing agents form the most effective group of sup-

pressants. FC-218, HFC-227ea, HFC-227ca, and HFC-236fa constitute the next most effective group, followed by the remaining hexafluoropropanes and the pentafluoropropanes. HFC-245ca is the least effective of the fluorinated propanes tested, but is more effective than FC-116 and HFC-125. The tetrafluoroethanes and SF_6 are only more effective than CF_4 and N_2 . The effectiveness ranking for methane, although similar to that of the other fuels, does exhibit some peculiarities. First, FC-116 appears more effective than most of the fluorinated propanes. Second, within the 3σ experimental uncertainty of ± 0.8 mole %, all of the fluorinated propanes tested containing less than two CF_3 groups are equal in their ability to suppress methane flames at 80 s^{-1} .

Although the relative effectiveness of the various suppressant groups is similar for all the fuels tested, the exact ranking within a group depends on the fuel. Furthermore, the rankings extracted from the counterflow data are somewhat strain rate dependent. The position of the SF_6 extinction strain rate curve relative to those of the fluorinated ethanes illustrates this dependence. Figure 3a shows that at strain rates between 400 and 500 s^{-1} , in a propane flame, SF_6 is more effective than HFC-125. Below 100 s^{-1} , it is less effective than both HFC-134 and HFC-134a. The extinction concentrations discussed in the present paper are all expressed on a molar basis. On a mass basis, the bromine- and iodine-containing agents are still the most effective suppressants, with all of the other agents tested, including N_2 , exhibiting similar effectiveness.

Effect of Fuel Type on Agent Extinction Concentrations

Figure 5 shows that fuel type has an impact on the magnitude of the extinction concentrations, but not on the effectiveness ranking of the agents tested. The extinction concentrations obtained in the four different fuels are compared for several agents in Fig. 6. Included are all of the agents tested in the n-heptane cup burner, with the exception of Halon 13001, Halon 1211, and Halon 1201. The agents are ranked in order of decreasing n-heptane effectiveness, with the

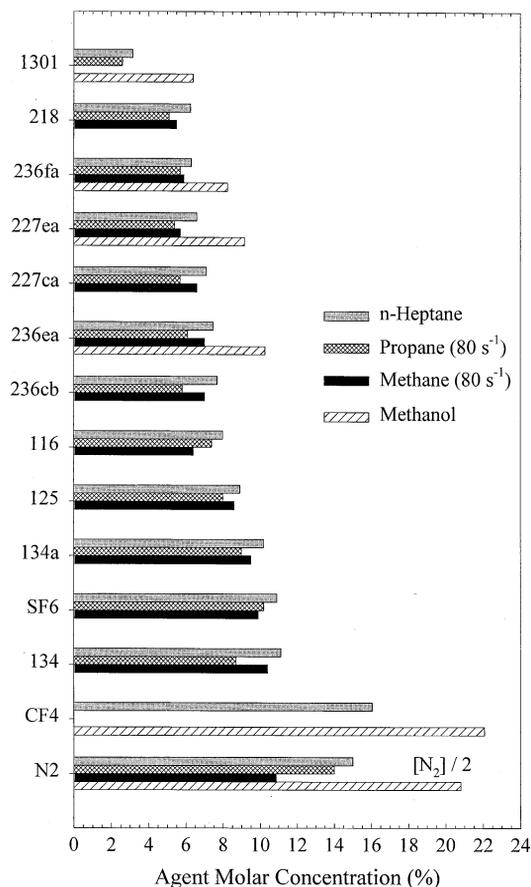


Fig. 6. Effect of fuel type on agent extinction concentration. The n-heptane and methanol data were collected in a cup burner. The methane and propane data were collected in a counterflow burner at a strain rate of 80 s^{-1} .

most effective agent listed at the top of the bar chart.

Figure 6 shows that, for the agents tested, methanol flames are more difficult to extinguish than the alkane flames. This is due in part to methanol's high sensible enthalpy of extinction relative to that of the alkanes. For all agents except Halon 1301, between 30 and 40% more agent is required to suppress methanol flames relative to the n-heptane flames. For Halon 1301, the required amount doubles. The greater reduction in the effectiveness of Halon 1301 can be attributed to a decrease in its chemical contribution to suppression. For n-heptane, chemical factors contribute 80% to Halon 1301's effectiveness. For methanol, they contribute 70%.

Extinction concentrations for methane and propane nonpremixed counterflow flames at 80 s^{-1} are similar to those for n-heptane cup burner flames. All 12 of the agents tested in both n-heptane and methane flames are more effective against the latter. The largest deviations between the two fuels occur with N_2 , 28%, and HFC-116, 20%. For 8 of the 12 agents, the deviations are less than 10%. In the case of propane, the largest deviations from the n-heptane values occur with HFC-236cb, 25%, and HFC-134, 22%. For 4 of the 13 agents tested in both fuels on Fig. 6, the deviations are less than 10%, with all 13 agents more effective in propane. Halon 1201 and Halon 13001 were the only agents more effective in n-heptane: 10% more Halon 1201 and 3% more Halon 13001 are required for propane flames. Counterflow experiments with both methane and propane at low strain rates yield extinction concentrations, in addition to effectiveness rankings, applicable to n-heptane cup burners.

CONCLUSIONS

The suppression effectiveness of four fluorinated ethanes, 10 fluorinated propanes, four bromine- or iodine-containing halons, CF_4 , SF_6 , and N_2 was investigated. Curves relating extinction strain rate to agent molar concentration were obtained for many of the suppressants in methane/air and propane/air nonpremixed counterflow flames. For the particular counterflow apparatus used, local strain rate was linearly correlated with an expression for global strain rate derived for plug flow boundary conditions. LDV velocity profile measurements were used to construct the correlation. This correlation is valid for methane and propane flames, with and without suppressants present.

The relative effectiveness of the fluorinated propanes correlates with the number of CF_3 groups in the agent's molecular structure. Effectiveness does not correlate significantly with any other structural feature. For agents with the same number of CF_3 groups, compounds with higher fluorine to hydrogen atom ratios are slightly more effective, particularly at low concentrations. These trends in effectiveness hold for fluorinated ethanes as well. The presence of

CF₃ groups also correlates with an enhanced suppression performance of agents that contain bromine. Numerical predictions of the flame speed of doped methane/air mixtures indicate that HFC-134a, with one CF₃ group, causes a greater reduction in flame speed than HFC-134. Analysis of the chemical kinetics indicates that the major removal pathway for HFC-134 is thermal dissociation, whereas those for HFC-134a are hydrogen abstraction by H and OH, and HF elimination. Kinetic sensitivity analysis indicates that these differences in agent consumption are primarily responsible for the predicted isomeric differences in flame speed reduction.

Overall, the fluorinated propanes are found to be more effective on a molar basis than the fluorinated ethanes. The greater effectiveness of the fluorinated propanes is consistent with their greater sensible enthalpy relative to the fluorinated ethanes. For the fluorinated propanes and ethanes studied, the chemical contributions to suppression did not exceed 35%. Bromine- or iodine-containing agents are more effective than either ethanes or propanes that contain fluorine as the sole halogen. These bromine- and iodine-containing agents suppress flames mainly through chemical means, with physical contributions to suppression not exceeding 30%.

The effectiveness ranking of the agents tested was found to be essentially independent of fuel type. Fuel type does have an effect on the magnitude of the extinction concentrations. Methanol flames are more difficult to extinguish than either methane, propane, or n-heptane flames. For Halon 1301, the agent concentration required to extinguish a methanol cup burner is more than double the amount required to extinguish an n-heptane flame. For HFC-236fa, HFC-227ea, HFC-236ea, CF₄, and N₂, 30 to 40% more agent is required. Propane and methane flames yield extinction concentrations that are more similar to n-heptane values.

This work was supported by the U.S. Naval Sea Systems Command. We thank Michael Davis, Michael Kozma, and Courtney Smith for assistance with the velocimetry measurements; and Philip Westmoreland for providing calculated thermodynamic data for HFC-227ea. We ac-

knowledge Great Lakes Chemical, Dupont, and AlliedSignal for providing samples of some of the agents.

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Received 17 March 1999; revised 1 September 1999; accepted 21 October 1999