# Understanding Combustion Promotion by Halogenated Fire Suppressants

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CASE WESTERN RESERVE

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## Goals

Understand the overpressure phenomena in the FAA Aerosol Can Test

- 1. Why is the overpressure occurring with the added suppressants?
- 2. What can be done about it?





FAA Aerosol Can Simulator

## Approach



Progress

#### Background

Thermodynamic Equilibrium Calculations Kinetic Mechanism Development Measurement of 2-BTP Decomposition Perfectly-Stirred Reactor (PSR) Calculations Diffusion Flame Calculations (Cup Burner) Homogeneous Auto-Ignition (PFR) Calculations Diffusion Flame Calculations (Counterflow) Premixed Flame Calculations (PREMIX)

# Background:

# Previous findings

#### Flame Extinction



Background:

Chemical Time:

$$\tau_c \equiv \rho / W = \rho c_F^{-n} c_O^{-m} A^{-1} \exp(E / RT).$$

Flow Time:

 $\tau_r = \ell / v$ 





#### - T<sub>aft</sub> is high for all η.

- Change in behavior at [X]/[H]=1 (about 7.5 % HFC-125, red curve above).
- With large amounts of agent, a wide range of  $\eta$  gives nearly equivalent T<sub>aff</sub>.
- As agent is added, more and more chamber volume is necessary to achieve stoichiometric combustion.
- Where flame goes out (X=13.5 %), all the chamber volume is involved in combustion (i.e., η=1).

2-BTP: Adiabatic Flame Temperature (T<sub>aff</sub>)

Thermodynamic Equilibrium Calculations



#### - $T_{aft}$ is high for all $\eta$ .

- most of the plot is below [X]/[H]=1 (about 6 % 2-BTP), so can't see change at [X]/[H]=1 .
- With large amounts of agent, a wide range of  $\eta$  gives equivalent T<sub>aft</sub>.
- As agent is added, more and more chamber volume is necessary to achieve stoichiometric combustion.
- Where flame goes out (X<sub>i</sub>=6 %), all the chamber volume is involved in combustion (i.e., η=1).



Halon 1301: Adiabatic Flame Temperature (T<sub>aft</sub>) Thermodynamic Equilibrium Calculations

- most of the plot is below [X]/[H]=1 (about 11 % CF<sub>3</sub>Br), so can't see change at [X]/[H]=1 .
- The amount of chamber volume for peak T<sub>aft</sub> does not change with X<sub>i</sub>.
- $CF_3Br + 2H_2O = 3HF + HBr + CO_2$ , -Why? =>
- -i.e., there's always enough H and O in the system to oxidize the CF<sub>3</sub>Br without more air!
- The  $T_{aff}$  is very sensitive to  $\eta$ .

# Thermodynamic Equilibrium Calculations

What do they tell us about the maximum pressure rise?

HFC-125: Predicted Pressure Rise

Thermodynamic Equilibrium Calculations



- The higher  $\eta$ , the greater  $\Delta P$  (more reactants, more heat release, more expansion of hot products—since the oxidizer also includes a "fuel" species).

- The actual fraction of chamber volume (oxidizer) which can react has a large influence on  $\Delta P$ .
- Equilibrium thermodynamics predicts the final pressure quite well.
- Why does the agent not reduce the extent of reaction?



Thermodynamic Equilibrium Calculations



- Equilibrium thermodynamics predicts the final pressure quite well.
- Why does the agent not reduce the extent of reaction?

Halon 1301: Predicted Pressure Rise

Thermodynamic Equilibrium Calculations



- Higher  $\eta$  has very little effect on  $\Delta P$ .

- At  $\eta$  of peak T<sub>aft</sub>, or CO<sub>2</sub>, the  $\Delta P$  is constant! => can't use pressure rise to determine  $\eta$ .

- Actual  $\Delta P$  is always less than predicted. This due to a chemical kinetic effect, but is it from Br or from reduced temperature (i.e., from mixing-induced dilution)?

=> MUST LOOK AT THE KINETICS TO FIND OUT!

Halon 1301: Predicted Pressure Rise

Thermodynamic Equilibrium Calculations



- As X<sub>i</sub> of agent goes up,  $\Delta P$  will increase for R-125 and 2-BTP, but not for 1301.

=> MUST LOOK AT THE KINETICS TO FIND OUT WHY!

## Kinetic Mechanism Development

CH4-air premixed flame, 0, 4, and 6 % R-125

Currently developing these charts for HFC-125 with propane and ACT.



# Kinetic Mechanism Development

#### Sub-Mechanisms

# Aersol Can Test Mechanism:

	Species	Reactions	
C <sub>4</sub> hydrocarbon mechanism from Wang	111	784	
Ethanol mechanism of Dryer	5	36	
HFC mechanism from NIST <sup>1,2</sup>	51	600	
CF <sub>3</sub> Br mechanism of Babushok (NIST) <sup>2</sup>	10	122	
	177	1494	

<sup>1</sup> Updated rates from more recent literature, additional rates of fuel radical reaction with R-125.

<sup>2</sup> Validation: CH<sub>4</sub>-air and CH<sub>3</sub>OH systems (with CHF<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>F<sub>4</sub>, C<sub>2</sub>HF<sub>5</sub>, CF<sub>3</sub>Br, C<sub>3</sub>HF<sub>7</sub>):

premixed flame speed,

- species profiles in low-pressure premixed flames,
- extinction strain rate for counterflow diffusion flames,

- cup-burner extinction.

Kinetic Mechanism Development :

Measurements of 2-BTP Decomposition

- Can't do calculations yet for 2-BTP because there's no mechanism for its initial decomposition.

- Once we have its decomposition to HFC and HBrC fragments, it will feed into the overall NIST HFC mechanism.

- So, we must first estimate/measure/calculate its decomposition.

Kinetic Mechanism Development : Measurements of 2-BTP Decomposition



# Single Pulse Shock Tube

#### Characteristics:

- System heated to 100 °C
- *τ* = (500 ± 50) μs (monitored with pressure transducers)
- Typical shock conditions: 2-6 bar, 900 – 1250 K

#### Advantages of Shock Tube for Gas Kinetic Studies:

- Essentially a pulse heater,  $\tau = (500 \pm 50) \,\mu s$
- No surface induced chemistry (diffusion slow compared with τ)
- Use of dilute conditions, radical chain inhibitors, sensitive GC/MS analysis
   → isolation of initial processes, observation of multiple channels

# Studies of 2-BTP Decomposition

#### Unimolecular (initial studies):

- HBr elimination from 2-BTP ca. 100x slower than unfluorinated analog
- Initial kinetic studies show some interference from radical induced decomposition (work in progress)
- Slow rate suggests importance of radical processes in practical systems

#### Bimolecular decomposition induced by reactive radicals (e.g. H atoms):

#### $H + 2-BTP \rightarrow Products$

- Initial studies show products indicating displacement and abstraction of Br as major channels.
- But product spectrum more complex than expected with some as yet unidentified species.
- Work in progress to determine mechanism and kinetics.



# Perfectly-Stirred Reactor (PSR) Calculations

- -Used to estimate the overall chemical reaction rate.
- Performed for R-125, 1301, and 1301 with N2.



#### Assumptions:

- specified premixed inlet conditions.
- adiabatic (no heat losses), no species reaction at the walls.
- perfectly stirred (outlet conditions are the same as the reactor conditions).
- steady-state operation.

# Perfectly-Stirred Reactor (PSR) Calculations

#### Calculation method



- 1. We want a measure of  $\tau_{chem}$
- 2. At the blow-out condition,  $\tau_{chem} = \tau_{flow}$
- To find the blow-out condition, calculate T<sub>psr</sub> at decreasing values of the residence time, τ<sub>flow</sub>, until the time is too short for reaction to occur (T<sub>psr</sub> drops to inlet temperature (blow-out).

# Perfectly-Stirred Reactor (PSR)

## Overall Chemical Rate with R-125



 $\label{eq:charge} \begin{array}{l} - \mbox{Adding R-125 lowers } \omega_{\mbox{chem}} \mbox{ for rich mixtures (low $\eta$), but raises (then lowers) it for lean mixtures (high $\eta$). \\ -\eta \mbox{ has a big effect on overall chemical rate at low $X_{\mu}$ less effect at high $X_i$ (follows temperature results). \\ - \mbox{ i.e., for higher $X_{\mu}$ these curves flatten ( $\omega_{\mbox{chem}}$ is insensitive to $\eta$ for $\eta > 0.4$ ). } \end{array}$ 





- Assuming a constant  $\omega_{chem}$  for extinction (reasonable first cut) implies  $\eta$  increases as X<sub>02</sub> decreases. => reasonable, but is it really true?

# Equilibrium and PSR Calculations Indicate:

=> In the FAA ACT with R-125 or 2-BTP, to achieve the observed pressure rise, a large fraction of the chamber volume (with the agent) must be involved in the combustion.

=> Thus, the agents are not inert, but rather, act like poorly-burning fuels.

=> Unlike in other flames, very little kinetic inhibition is occurring with R-125 and 2-BTP; whereas,  $CF_3Br$  does inhibit the flame, as expected.

=> The amount of chamber volume involved in the combustion,  $\eta$ , appears to be a key parameter controlling the behavior (i.e., the kinetic inhibition by CF<sub>3</sub>Br is very sensitive to  $\eta$ , but R-125 is not).

Simulations with 2-BTP should be able to tell us why 2-BTP, which has a Br, does not inhibit the flame (but is expected to).

# Diffusion Flame Calculations (Cup Burner)

# 0 % CO<sub>2</sub>







Diffusion Flame Calculations (Cup Burner):

**UNICORN** Simulations

#### UNICORN

#### (UNsteady Ignition and COmbustion with ReactioNs)

Time-dependent, axisymmetric reacting flows are simulated by solving full Navier-Stokes equations.

Momentum Equations --- QUICKEST Scheme (3rd order accurate in time, 4th order accurate in space)

Pressure Field --- Direct solution of Poisson Equations

Species and Enthalpy --- Hybrid scheme of Upwind and Central Differencing

Turbulence---- k-& model

Radiation---- Optically thin-media assumption

Soot---- Detailed kinetics for gas phase and a two-equation model for solid phase

Detailed Chemistry Models.





Diffusion Flame Calculations (Cup Burner)

Diffusion Flame Calculations (Cup Burner):

Goals

Cup burner calculations can tell us :

- 1. What is the inerting concentration for ACT fuel, and why?
- 2. What is happening to the flame chemistry as X<sub>i</sub> increases, for 1301 or R-125?
- 3. How does agent react in a partially-premixed environment?



Diffusion Flame Calculations (Cup Burner)

Results



Diffusion Flame Calculations (Cup Burner)

Results





Propane-air ACT<sub>fuel</sub>-air



<sup>1</sup>% by volume.

Anon. (2004)

Anon. (2004) Kondo et al. (2009)

Calculated MECs This study (1g<sub>n</sub>)

This study (0g)

Linteris (1995, 2007),

Mean

Mean

Measured Inerting Concentrations Moore et al. (1995)

Linteris et al. (2007)

<sup>2</sup>A gas mixture of propane, 15.9 %; ethanol, 45.4 %; and water, 38.7 % by volume <sup>3</sup>Abrupt blowoff.

8.7

8.8

4.3

3.67

6.2

6.2

2.86 8.6

2.59<sup>3</sup>

10.2

10.25

15.7

14.8

15.25

15.1

3.65

2.22 9.05

1.85<sup>3</sup> 16.2

3.1

3.12 8.88

# Propane with R-125

Propane with R-125



## Premixed Flame Calculations (Counterflow)



# Propane with R-125

#### Propane/Air Opposing Jet Diffusion Flame

	X <sub>R-125</sub>  ext (Calculated)		X <sub>CF3Br∣ext</sub> (Calculated)	
100	0.075	~0.077	0.021	~0.022
250	0.039	~0.04	0.014	~0.015
500	0.0092	~0.01	0.0018	~0.0018

Air-side strain rates Agent was added to the air jet

- Experimental and simulated (UNICORN) extinction conditions in the counterflow diffusion flame (propane) agree well.

- This gives us confidence in the mechanism, and the numerical simulations, so they can be used to understand the overpressure causes.

# Homogeneous Auto-Ignition Calculations

Used to estimate the time to ignition for a homogeneous mixture of reactants (describes the ignition propensity; i.e., ignition chemistry can be different from flame chemistry).

#### Assumptions:

specified premixed inlet composition, T<sub>init</sub>, and fixed P.
adiabatic (no heat losses), no species reaction at the walls.
homogeneous mixture (no transport).
time-varying behavior.



# ACT Fuel Only





# Summary of Progress

- 1. Literature reviewed.
- 2. Thermodynamic data obtained.
- 3. Kinetic mechanism for R-125 assembled, tested, updated.
- 4. Thermodynamic data for 2-BTP
- 5. IR emission data for HF, and COF<sub>2</sub>.
- 6. Wrote pre- and post-processors for all the numerical codes.
- 7. Initital shock-tube results for 2-BTP decomposition obtained.
- 8. Calculations (finished or in progress) for R-125:
  - -Equilibrium
  - -PSR
  - -Ignition
  - -Counterflow burner
  - -Cup burner
  - -Premixed
- 9. FAA ACT data obtained and compared with above.
- 10. New test chamber
  - -specified, drawn, in machine shop -sensors ordered and/or obtained -Image analysis program written

## **Future Plans**

- 1. Perform further analysis of simulations in progress to understand reasons for lack of kinetic inhibition with R-125.
  - Perform 2-D, axi-symmetric, unsteady simulations for a turbulent fuel jet to understand the effects of mixing on the extinction.
  - Repeat existing calculations at higher pressure.
- 2. Perform large-scale tests in cooperation with the FAA Technical Center to test our understanding.

#### 3. 2-BTP:

- measure and estimate decomposition rate
- develop kinetic mechanism
- perform calculations
- analyze results to understand lack of kinetic effect with 2-BTP
- 4. Develop a new laboratory-scale experiment to:
  - validate our understanding (e.g.,  $\eta,$  pressure effects), and the mechanisms.
  - explore range of conditions for which inhibition/enhancement occurs
  - rapidly screen new agents.
- 5. A Ph.D. student, and a Prof. at U. Maryland have applied for a NIST/ARRA Fellowship to work on this problem.

# New Constant-Volume Combustion Device



Photo Courtesy of Prof. Li, Purdue

Key Questions Still to Answer

- 1. Is the amount of involved oxidizer the key feature?
- 2. Does the agent reaction rate affect the strain conditions in the FAA ACT?
- 3. Why are the kinetics with R-125 not slower (i.e., slow enough for extinguishment)?
- 4. Does Br help slow the kinetics with 2-BTP?
- 5. Is the overpressure due to a pressure enhancement of the agent flammability?
- 6. Is the inerting concentration required for suppression?
- 7. Is there any way around the undesired results?

**New UNICORN Simulations** 







Questions?

# Publications

Katta, V.R. et al. "Effects of halon replacements on burning characteristics of test fuels." to be presented at the 49<sup>th</sup> Aerospace meeting in Orlando, 4-7 January 2011.

Linteris, G.T., Takahashi, F., Katta, V.R., and Chelliah, H.K., "Thermodynamic analysis of suppressant-enhanced overpressure in the FAA Aerosol Can Simulator," to be submitted to *Fire Safety Science -- Proceedings of the Tenth International Symposium*, International Association of Fire Safety Science, 2010.